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GYULA GRASSELLY

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Szerkeszti
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Kiadja
a József Attila Tudományegyetem Ásványtani, Geokémiai és Kőzettani Intézete
Szeged, Táncsics Mihály u. 2.

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50 YEARS OF THE INSTITUTE OF MINERALOGY, GEOCHEMISTRY AND PETROGRAPHY OF THE ATTILA JÓZSEF UNIVERSITY AT SZEGED

GY. GRASSELLY

University education and research in geology and petrography in Szeged started in 1921 when, after World War I., József Ferenc University found its home in this city.

On reviewing the past fifty years, we can look back on a continuous development which was only interrupted and retarded by World War II., and which, after the War re-started from almost zero level to proceed towards an unprecedented achievement.

On the occasion of the 50th anniversary, we pay homage to our predecessors, the directors and co-workers of Institute, who not only began teaching and scientific

PROFESSOR DR. ZSIGMOND SZENTPÉTERY (1880—1952)
first director of the Institute, between 1921—1940

activity with their knowledge, energy and love of their field, but also established those foundations and means that are the basis for further activity and development even today.

Between 1921—1940, the Institute bore the name *Institute of Geology and Mineralogy*, and the members of the Institute achieved — under the leadership of the first director of the institute, PROF. DR. ZSIGMOND SZENTPÉTERY (1880—1952) — valuable results principally in the field of petrography and geology.

PROFESSOR SZENTPÉTERY, in his activity associated with Szeged, dealt mainly with the petrography and geology of the Bükk Mountains, and partly with those of the Börzsöny Mountains; he founded the petrographical and mineral collection of the Institute, and, in cooperation with other professors of the Faculty, founded the forerunner of Acta Mineralogica-Petrographica, the "*Acta Chemica, Mineralogica et Physica*", in which were published a great number of his and his co-workers' studies on the results of their research.

At that time the Institute had the equipment necessary to fulfil the requirements of education of mineralogy, geology, and — mainly descriptive — petrography. After PROFESSOR SZENTPÉTERY's death, his scientific activity was reviewed by ENDRE LENGYEL in 1952 [E. LENGYEL: A Reminiscence of Zsigmond Szentpétery, Földt. Közl., **82,** 113—118], including a detailed bibliography.

The academic year 1940/41 came as a turning-point in the life of the Institute. PROFESSOR SZENTPÉTERY transferred to the University of Kolozsvár, and the old institute gave birth to two new ones at Szeged: the *Institute of Geology and Palaeontology;* and the *Institute of Mineralogy and Petrography*, to the directorship of which SÁNDOR KOCH was appointed. He had already worked 23 years at the Collection of Minerals of the Hungarian National Museum, world-famous in its golden age.

The new director, PROFESSOR SÁNDOR KOCH brought with him not only his enormous knowledge and his love of mineralogy acquired at the Museum, but also his enthusiasm about science and about anything that could make human life more beautiful and free from care. The whole of his character and his personal magnetism make it understandable that he brought a new human atmosphere as well as a new point of view of scientific approach to the department, the conservation and further maintenance of which is an honorable duty of his followers.

The author of these lines began his career at the side and under the leadership of PROFESSOR KOCH in 1941, and understandably enough, he cannot and does not even want to write about this period of Institute with impersonal neutrality, because he recieved incentive both for his career and personal development from his predecessor, PROFESSOR KOCH.

The starting of education and research activity at the new, independent Institute of Mineralogy and Petrography needed significant reconstruction of the curriculum and of the range of research as well as of the supply of equipment. PROFESSOR KOCH did his best to continue petrographical research in accordance with the precept of the SZENTPÉTERY school, but the former mineralogical and petrographical research — mainly of descriptive character — was gradually replaced by the more modern mineralogical-geochemical trend.

At that time students had no access to Hungarian text-books on mineralogy and petrography, — as they have now— therefore, the first thing to do was to supply the students of the Institute with suitable lecture—notes, and to ensure the conditions necessary for an up-to-date education of mineralogy, crystallography, and petrog-

raphy. It took several years' efforts to establish all this and, when World War II. had come to an end, hardly anything of the achievements remained.

However, something remained that could not be damaged: the firm belief that education must be resumed, research must be continued and everything that was destroyed must be recreated. Thus, in the autumn of 1945, life of the Institute began

PROFESSOR DR. SÁNDOR KOCH (1896—),
director of the Institute between 1940—1968

again. Although there was no heating in the lecture hall, lecturers and students were enthusiastic, and their unselfish and generous cooperation was a great help to the Institute in recovering from the effects of war.

Following the time of reconstruction, the Institute has continually been developing, under slowly but steadily improving research conditions. These years the main emphasis in the field of research has been on studying minerals and their deposits in Hungary. The monograph "*The Minerals of Hungary*" by SÁNDOR KOCH [1966] is the first Hungarian work of its type, which, on the basis of SÁNDOR KOCH's and partly his co-workers' scientific activity of several decades, gives a general picture of the mineral resources and deposits in Hungary and, based on a unified genetic viewpoint, offers a great help to experts of both the present and the future.

It was those years, too, that manganese ore research started at the Institute directing the main attention to the Hungarian sedimentary manganese oxide ore deposits, then treating in general the thermal behaviour of various manganese oxides. Petrographic studies have also continued, especially by the research of the metamagmatites of the Mátra Mountains, and, beside the former approach of a rather descriptive nature, the genetic aspects have received more importance.

Significant development has been shown by the Mineral Collection of the Institute *(Fig. 1)*, as the old systematic collection has been renewed and largely supp-

lemented by the addition of PROFESSOR KOCH's private collection, the foundation of which he laid in his youth and which he was ceaselessly enriching all during his active service. In fact, PROF. KOCH's name is associated with the description of

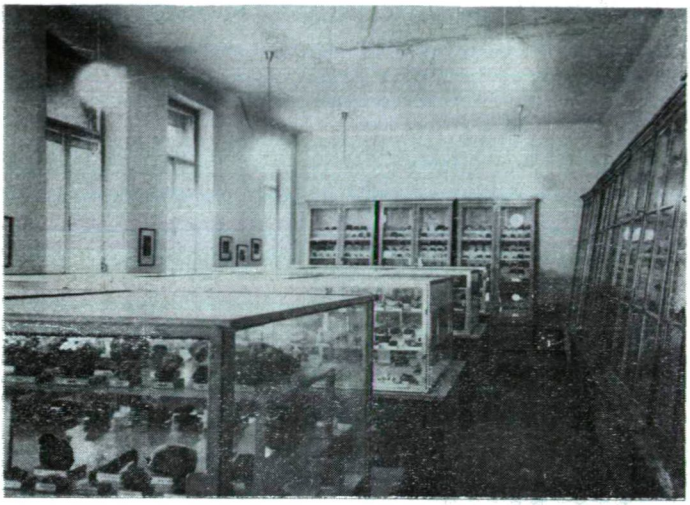

Fig. 1. The mineral collection of the Institute: the Koch-collection and the systematic mineral collection

fülöppite (3 PbS. 4 Sb_2S_3) from Baia Mare (Rumania), with that of a mineral — indicated as an unknown bismuth telluride by K. SZTRÓKAY — as *csiklovaite* (Bi_2TeS_2 from Nagybörzsöny, Hungary), and with the description of *mátraite* (ZnS 3 R-type from Gyöngyösoroszi, Hungary), as well as of *kiscellite* (a fossil resin from Mt. Remete, in the neighbourhood of Buda, Hungary).

The *Koch-collection* is a representative collection of the characteristic minerals of the once world-famous mineral occurrences of the Carpathian Basin, and, as such, the Mineral Collection of the Institute stands among the first in the country, presumably not as to its volume but as to the selection, beauty, and representative display of its samples. The petrographical collection and that of the raw-materials are smaller in size, but highly suitable for the purposes of education, and are constantly developing as well as the mineral collection, both mainly by exchange.

This period of the Institute is also associated with the initiation of the new periodical, the *Acta Mineralogica-Petrographica*. The first copy of the publication was issued in 1943, then, after an interruption caused by the war, it has been appearing year by year since 1948, at first in Hungarian, with abstracts in foreign languages, while later, almost exclusively in English. The publication was issued and edited by SÁNDOR KOCH until 1968. From 1968 on, it has been published under the editorship of the author of this reminiscence, who cooperated in editing the Acta during the preceeding 10 years as well.

In the past, the Acta Mineralogica-Petrographica used to serve almost exclusively as the publication of the members of the Institute, while in recent years, it has regularly included papers by foreign authors, too. The Business Meeting of the Working

Group on Manganese Formation of the International Association on the Genesis of Ore Deposits, held in Tokyo in 1970, accepted it as a semiofficial periodical of the Working Grup, accepting and including papers by the authors of the Working Group treating the field of manganese ore research, and summaries and reviews on the results of manganese ore research in differente countries.

The exchange of the Acta Mineralogica for other periodicals has been a great contribution to the collection of periodicals of the Institute, comparatively extensive today. We receive 120 periodicals from 24 countries, mainly through exchange *(Fig. 2)*, and to a smaller degree by subscription.

The volume of the library, too, is regularly developing, and the books most necessary for special research at the Institute are all at the researchers's disposal. The number of catalogued books makes more than 2000 volumes, and there is a collec-

Fig. 2. Part of the periodicals collection of the Institute

tion of several thousand reprints, the most important part of these being the collection of mineralogical articles related to mineral occurrences of the Carpathian Basin *(Fig. 3)*.

Due to the changes in the system of education, and in accordance with the requirements of practical life, the range of education and research has more and more shifted in the direction of geochemistry. This was expressed by the change of the name of the Institute in 1964. From that time on, the Institute has had the name *Institute of Mineralogy, Geochemistry and Petrography.*

In 1968 a change occurred in the leadership of the Institute. Since then the head has been the author of the present lines. PROFESSOR KOCH retired at the age of 73, in 1969, after 50 years of meritous educational and research work, leaving a rich and compelling heritage to his follower and to the whole of the Institute. A selected bibliography of his activity was published in the Acta Mineralogica-Petrographica [1966, **17,** p. 69—75].

PROFESSOR KOCH *is completing his 75th year at the time of the appearence of this volume of the Acta, and these lines are also intended to congratulate him and, first of all, to thank him for all he taught us, his disciples and co-workers. We, who*

were then beginners, were taught by him, by his personal precept even without words that education work is the first and foremost task of the University, and that a teacher is obliged by his profession to be concerned with the students, with the formation of

Fig. 3. Part of the library of the Institute

their character as well as their progress in their scientific work. He also impressed on us that besides knowing the new results in our own fields, we must also be acquainted with those imperishable values that human creative spirit attained in other fields, as in that of literature and art.

The consequence of these influences and impressions is that his former pupil has remained a disciple even if his close scientific activity has developed in quite a different direction from that of the teacher, who paved the way for his pupil with a helping hand.

Fig. 4. The lecture hall of the Institute with the collection displaying the utilizable rawmaterials of Hungary

From 1968 the Institute has undergone a significant reconstruction. The lecture halls *(Fig. 4)* and the laboratories badly needing innovation have been rebuilt with a considerable financial support of the University. About 1950 the "laboratory" still had the same appearance (seen in *Fig. 5*) as at the end of the 30ies, while now it has been replaced by up-to-date laboratories, an analytical and an experimental one as seen in *Figs. 6, 7*, an extra laboratory has been installed for the purposes of thermal research *(Fig. 8)*; we have established the X-ray and spectrographical laboratories and a room for the preparation of the material to be studied *(Fig. 9)*, as well as two smaller laboratories and an electrotechnical workroom.

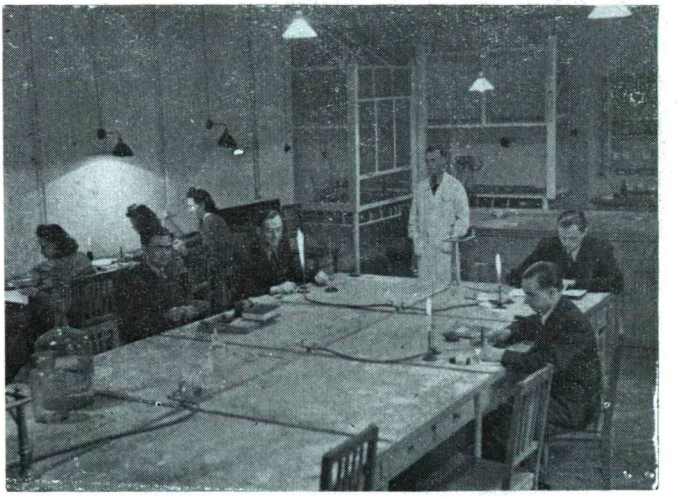

Fig. 5. „Laboratory" in the 1930ies

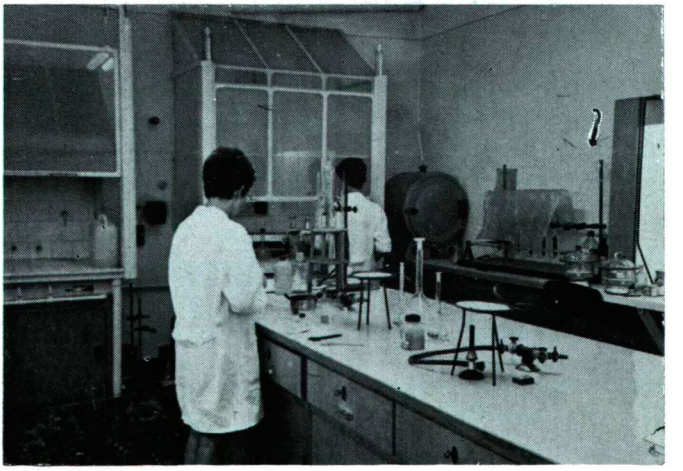

Fig. 6. The new analytical laboratory built in the place of the old one

All these reconstructions were mainly recquired by the change of education and research program in the direction of geochemistry and, in accordance with this, by the instrumental equipment developed from 1957 to a more and more noticeable

Fig. 7. The experimental laboratory established in the place of the old „laboratory"

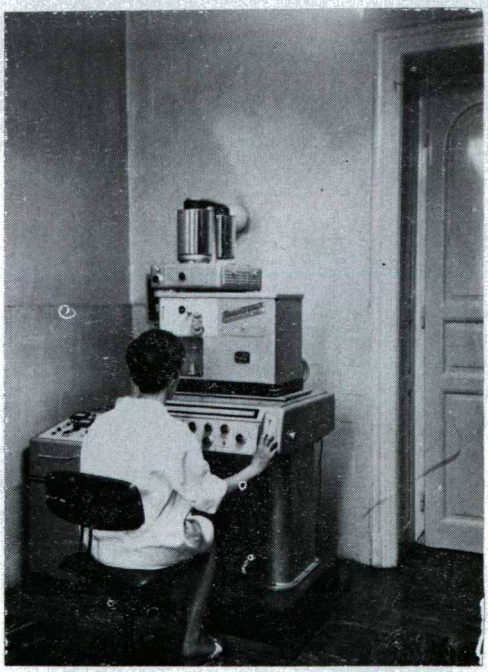

Fig. 8. „Derivatograph" for the simultaneous registration of T, TG, DTG and DTA curves, with programmed heating

degree. At present we have conditions for any possible research activities at the Institute ranging from spectrographical study of trace elements, X-ray and thermal studies to various instrumental experiments. At the same time, the reconstruction has ensured convenient working conditions for the researchers and students, this also being a non-negligable aspect.

The present tasks of the Institute in the field of education are quite wide in range. We offer lectures on subjects in accordance with the character of the Institute for students reading for a secondary school teachers' diploma in biology-chemistry, chemistry-physics, and also for those students of chemistry and physics not specializ-

Fig. 9. Preparation room

ing in teaching. The lectures held regularly include those on mineralogy, crystal chemistry and petrography, together with the corresponding laboratory and field training.

Beside the obligatory lectures mentioned, the students can have a free choice of numerous other lectures dealing with special subjects, such as general geochemistry, organic geochemistry, mineral raw-materials in industry, research methods of geochemistry etc. Beyond these lectures, we regularly organize laboratory training for fifth-year students majoring in chemistry.

An important, though not the only, determining factor in the progress of the research activity of the Institute is the relation — recently become strong and close — between problems arising from the requirements of industry and practical life, and research at the Institute. The fact that in recent years rich hydrocarbon deposits

have been explored in the close vicinity of Szeged, has had an influence on the work of the Institute. Thus, one of the topics deals with the organic matter contents of sedimentary rocks, and with the carbonate and clay mineral contents of reservoir and non-reservoir sediments, and with the problem of the redox capacity of sedimentary rocks.

Another topic is given by the manganese ore research started earlier. In the foreground of research at present is the study of the role played by the various mangenese compounds in the migration of elements; by studying the adsorption characteristics of the different natural and artificial manganese compounds. Also associated with the research of manganese ore are the model experiments concerning, on the one hand, the solution and oxidation of manganese carbonate ores in Hungary and, on the other hand, the mechanism of the formation of manganosite.

The research of petrographical nature includes mainly that of the relation between ore formation and potassium metasomatism in the Mátra Mountains, as a continuation of earlier research of the metamagmatites of the Mátra Mountains.

We continue our activity in the hope that, during te next years, the Institute will not only maintain, but also develop all the results which the predecessors have achieved and which have also been contributed by the present co-workers of the Institute, and that for the young researchers of the Institute and all those engaging in this work later on we will be able to provide still better conditions than those we had when began our career; and we also hope that we will leave them a professional and intellectual heritage as good as the heritage we received from our predecessors.

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Acta Mineralogica-Petrographica, Szeged, XX/1, 13 — 17, 1971

THE THREE DECADES OF THE DEPARTMENT OF GEOLOGY, ATTILA JÓZSEF UNIVERSITY, SZEGED

K. BALOGH

The independent existence of the Department began in the autumn of 1940, when with the splitting into two of the Department of Mineralogy and Geology, which had functioned since 1921, it was separated from the Department of Mineralogy and Petrography. As for the initial condition and aims of the Department at the moment of gaining independence, let us refer the reader to the paper of ISTVÁN FERENCZI [1943, 1944], as no paper of this kind has been written ever since. In the following discussion let us review the history of the Department, for its experience may provide evidence determining its future.

THE CHANGES IN THE TASKS OF EDUCATION

Before 1947 the Department had two tasks to fulfil in education. On the one hand, secondary school teacher candidates, to be specialized in natural history and geography, were taught geology and paleontology according to a syllabus prescribed by the Institute for Training Secondary School Teachers. On the other hand, the Departments was training those students in geology and paleontology, which would not obtain a secondary school teacher's diploma and were just listening to lectures and attending exercises they were interested in during their studies in the university. These students completed their studies by compiling their Ph. D. thesis and passing their examination for doctorate.

Of course the lectureships of the two different types of teaching overlapped often each other. In possession of university absolutorium the teacher candidates were allowed to prepare a Ph. D. thesis and pass an examination for doctorate, if they wished, and still had power enough for doing so after passing their compulsory examinations for the teacher's diploma, or even without having obtained this. This last-mentioned means of training was less favourable for specialization. And yet, it was rather popular for enabling one to obtain two diplomas at the cost of prolongating one's studentship for a little time. From the point of view of the educational policy, it had the advantage of providing the secondary schools with natural sciences teachers of a wide range of knowledge, familiar in the domain of mineralogy and geology as well. In addition, however, because of difficulties in finding proper jobs, most of the graduates which became later geologists, had begone their career as secondary school teachers, too.

This situation was fundamentally changed by the concentration of the training of geologists at the L. Eötvös University in Budapest and the Technical University

of Heavy Industry at Miskolc (1948). However, the Department under consideration was yet more sensibly affected by the stopping in 1954 of the (five-year) training of teachers specialized in geography and geology that was introduced in 1950. Since the afore-mentioned date the "ex offo" teaching activities of the Department have been reduced to participate in the foundational training of the various secondary school teacher's specializations (biology—geography, mathematics—geography, foreign language—geography and biology—chemistry) and to organize timely special courses. Consequently, the Department has been deprived practically of the possibilities to traine oneself the specialists needed for the reinforcing of its own staff.

Only from 1964, this situation was altered in consequence of the claim to speeding up the training of specialists for study of flatlands and for hydrocarbon- and water-prospecting. Since that time the Department of Geology (in a common programme with the Department of Mineralogy, Geochemistry and Petrography) has allowed a few teacher candidates specializing in geography or biology or chemistry to obtain, after 3 years of education, a teacher's diploma in geology—chemistry, geology—geography or geology—biology, respectively. The education is facultative, being dependent on application and the Dean's permission. That is why courses of this kind are not started every year.

During the three years our students attend lectures (and take part in relevant exercises in practising) on general geology, historical geology, applied geology, general and systematic paleontology and the geology of Hungary on the one hand, and special courses in geophysics, hydrogeology, petroleum geology and geological mapping on the other.

The students participating in this special kind of education prepare their theses devoted to one of the geological disciplines. In general, they are trained in the domain of sedimentology so amply and thoroughly that they are entitled to carry out investigations of deep-drilling materials and analyses in laboratories of sedimentary petrography independently.

THE EQUIPMENT OF THE DEPARTMENT

30 years ago the equipment of the Department was rather poor, limited to a few microscopes and the most important instruments and devices necessary for working on the field (hand-operated drilling equipment) and in geological laboratories (chemical and granulometric analyses). The degree of equipment has since increased by leaps and bounds, particularly so in the last five years. The improvement of the Department's equipment enhances in the first place the possibility for conducting sedimentological investigations.

The Department's collections serving for both educational and research purposes, together with the demonstrating and documenting materials, have undergone a similarly significant progress. The old demonstrative plates have been replaced by a rich inventory of slides depicting the subject of every lecture being delivered. Even though the Department's collections cannot be amplified because of limitedness of the placement to such an extent as to cover the entire scope of the Department, efforts are being made to enhance their efficiency in their serving as a tool of education and as a model to work on before the students enter into service in practical life.

A special collection has been assembled to include primarily materials devoted to educational purposes for the students. In this collection the materials for visual

demonstrations, such as slides, thin- and polished sections, photographs and descriptions are represented by several copies.

A separate collection has been reserved for selected materials with photographs and written explanations giving a review of various subjects such as general and systematic paleontology, general geology (mainly sedimentology) and the geology of Hungary. This exhibition is of great significance also for public education, as no similar collection is available in the City Museum of Szeged. This fact also justifies the necessity to develop this collection into a duly illustrated, didactical exhibition which would be capable for fascinating a layman visiting it, that is into something like KOCH's Mineral Collection exhibited to the wide public at the Department of Mineralogy, Geochemistry and Petrography.

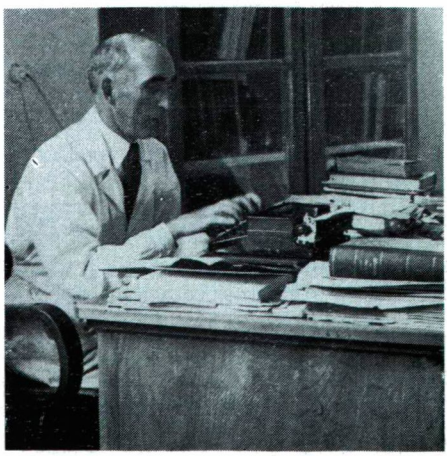
Finally, the research collection comprises the rock and fossil samples identified or used for comparisons by the staff of the Department.

To illustrate the development of the Department's Library, including both books and periodicals, let us recall that the number of books available at the Department at its birth 30 years ago was as low as 253 — a striking contrast to the 500 volumes growth of the last five years. The collection of off-prints has increased markedly too, attaining thrice the initial figure by the end of the third decade. Whereas 90% of the initial collection were papers of local, Hungarian, interest, the present-day collection embraces a comparatively wide spectrum of geology, paleontology and geophysics. The collection of periodicals has undergone a considerable progress, too. Whereas in 1940 the Department was receiving just a few journals, a total of 21 periodicals, Hungarian and foreign, are available to its staff now.

RESEARCH WORK

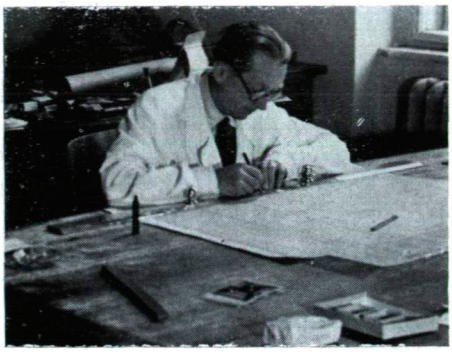
During the past 30 years the Department was directed by:

PROF. DR. ISTVÁN FERENCZI	from 1940 to 1944
ASSISTANT PROF. DR. ISTVÁN MIHÁLTZ	from 1944 to 1946
PROF. DR. FERENC HORUSITZKY	from 1946 to 1950
PROF. DR. ISTVÁN MIHÁLTZ	from 1950 to 1964
ASSISTANT PROF. DR. LÁSZLÓ JAKUCS	from 1964 to 1966
PROF. DR. KÁLMÁN BALOGH	since 1966



Prof. Dr.
Ferenc Horusitzky

Under the direction of the above, the members of the staff have from the very beginning conducted valuable scientific activities in spite of their modest number. The orientations and nature of these activities have been defined by the specialization and special scope of interest of the heads of the Department, by local conditions and by the requirements of practical life, all combined. Because of Szeged's situation in the Great Hungarian Plain (Alföld), most of these studies have been aimed at getting acquainted with the stratigraphy and lithology of the recent, Late Quaternary formations of the immediate vicinity and its wider environs. Undertaken by ISTVÁN MIHÁLTZ and his disciples, this work was connected with such vast projects as the canalization of the city of Szeged, defining the track of the Danube—Tisza Canal (which has not been executed as yet), locating the Tiszalök Hydroelectric Power Plant, and the Great Plain mapping programme launched by the Hungarian Geological Institute, Budapest. Consequently, the economic funds for the reasearch work were provided by city planning, agricultural and water supplies management organizations. The great merit of MIHÁLTZ and his disciples consists in the precising of the genetics of the 15 to 30 m thick epidermis of the Great Plain by granulometrical and palynological methods. After the micromineralogical investigations of the materials of a few comparatively deeper boreholes, the source directions of the Pleistocene and even Pliocene sediments were also explored and sketched.



Prof. Dr. István Mihált

What cannot be denied nevertheless is that the Department's scientific scope was markedly restricted as compared to FERENCZI's first programme. Let us recall in this connection that, beside investigating surficial geology, FERENCZI intended — very correctly — to investigate the entire Tertiary basin fill and, indeed, the pre-Tertiary basement as well. His intentions, however, were forgotten after his leave to abroad. With the decline of the vast campaigns for mapping, canalization and water power developments the first symptoms of the disadvantage of the biased specialization in unconsolidated sediments were felt as early as the middle of the 1950's. In the subsequents years, to 1965, the poorly equipped, small-staff Department had nothing else to rely on than the modest special-purpose credits provided by the government and the Academy of Sciences. These subventions, however, were enough merely to cover the expenses for summarizing earlier results and undertake investigations in part-themas. That was the moment when the Department joined the programme of complex investigations of the Great Plain's natron lakes. In addition, attempts were made at sedimentological evaluations of some core-drilled boreholes which have cut across the basinal Pleistocene and Upper Panno-

nian. These attemps, however, were jeopardized by the enforcing of the development of well-logging profiles, as the number of core-drillings and the amount of the material suitable for analyses had dropped to minimum.

This situation was changed radically by the great succes of oil and gas prospecting in the vicinity of Szeged. A city of merely agricultural interest, Szeged became overnight one of the country's most important industrial power centres. These changes in the economic background should be naturally reflected by corresponding changes in the Department's scientific programme.

Hydrocarbon prospectors take interest first of all for the pre-Quaternary basinfilling and its pre-Tertiary basement. This means that the Department's earlier tapered sedimentological activities have to be significantly widened by varied and modern investigations of facies of more diagenized detrital, carbonate and mixed-origin sediments. Thanks to the generous support on the part of the National Oil and Gas Trust the relevant methodological materials have been assembled for the most part. Thus the Department is already able to make efficient contributions in sedimentological respect to those investigations which the Trust is going to undertake in order to assess the prognostic oil and gas reserves of the country.

There is no question of breaking with investigations of the Quaternary formations either, for these will be carried on at a rate depending on the size of the expected sponsorship on the part of the Szeged Commission of the Academy. And yet, most efforts are to be concentrated on those complex sedimentological projects which are to be developed according to the contracts concluded between the National Oil and Gas Trust and the Department.

Based on local traditions and brought into correspondance with the needs of economy and the present-day level of science, this widening of the Department's scientific scope is useful and necessary for both the Department's staff and for raising education standards. It is hoped to endow our Department with such individual features which permit its rejoining in the under- and post-graduate training of geologists, over that of teachers, too, — opening up a new page in its history.

LITERATURE

FERENCZI I. [1943]: A szegedi M. Kir. Horthy Miklós-Tudományegyetem Földtani Intézete. — Földtani Értesítő **8**, 2, pp. 53—61. Budapest. (In Hungarian.)

FERENCZI I. [1944]: Beköszöntő. — Zum Geleit! — Geologica Szegediensia. **1.** Szeged, pp. 1—22. (In Germanian, with Hungarian summary).

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Acta Mineralogica-Petrographica, Szeged XX/1, 19–30, 1971

THE ISOPACHYTE MAP OF THE OLIGOCENE OF NORTH HUNGARY

K. BALOGH

INTRODUCTION

The Hungarian occurrences of the Oligocene are confined to three geological units: *1.* the Paleogene Basin of North Hungary—South Slovakia; *2.* the Karád—Buzsák Region; *3.* the so-called "Great Plain Flysch Belt" *(Fig. 1)*. The last-mentioned two have been explored only by wildcatting and are not yet known satisfactorily. Therefore only the North Hungarian Oligocene is discussed here.

The North Hungarian Paleogene has been the subject of detailed geological—paleontological investigations for a century. Such an interest was initially stimulated mainly by the presence of Eocene, Lower and Upper Oligocene brown coal deposits

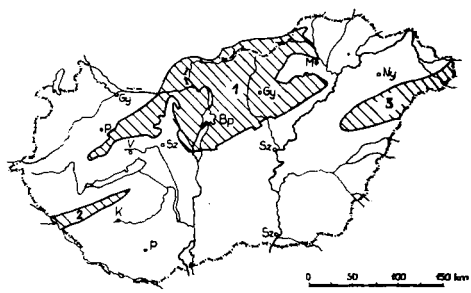

Fig. 1. The occurrences of the Oligocene sediments in North Hungary. *1.* The North Hungarian — South Slovakian Paleogene Basin. *2.* The Karád—Buzsák Region. *3.* The so called Great Plain Flysch Belt.

and since the 1930's by the prospective exploitation of oil and gas fields supposed and then really discovered in the Middle Oligocene of the eastern basin portions. Because of the block-faulted tectonics; the close similarity between the Upper Oligocene and Lower Miocene lithofacies; the extreme disproportions in the distribution of entirely core-drilled boreholes and the slow progress observable throughout Europe in the improvement of stratigraphical-paleontological methods, it was not until now that the geologists have arrived at gaining a clear knowledge of the virtual stratigraphic range of the Paleogene units under consideration. However, the road leading to this knowledge has been paved by the continually reviving "boundary discussions" aimed at both defining the Eocene—Oligocene and Oligocene—Miocene boundaries and correlating the Eocene subbasin fillings.

Out of the problems arisen in this connection it is the Chattian—Aquitanian problem that seems to be most significant owing to the great thickness of the sequences involved. As a result of coordinated efforts of Hungarian, Slovak and Austrian specialists [I. CSEPREGHY-MEZNERICS, T. BÁLDI, J. SENEŠ, M. VAŇOVÁ, A. PAPP] the CONFERENCE ON NEOGENE STRATIGRAPHY, Budapest 1969, provided evidence confirming the following conclusions [T. BÁLDI, 1969, T. BÁLDI, GY. RADÓCZ, 1969]:

— the deposition of the undoubtedly Middle Oligocene ("Rupelian") *Kiscell Clay* ("Kiscellian") and the beginning of the Miocene are separated just by one depositional unit;
— this unit is the "*Eger Formation*" ("Egerian") corresponding to the Upper Oligocene ("Chattian") and recommendable as its stratotype for the central Paratethys;
— synchronous with the Eger Formation, but of different facies, are the "*Törökbálint*" ("Kováčov"), "*Mány*" and "*Mór*" *Formations;*
— the sediments which overlie the Upper Oligocene thus determined and which used to be named "Chattian—Aquitanian", already belong to the Lower Miocene;
— the "Chattian—Aquitanian" formations under consideration, united under name of "*Salgótarján Formation*" by T. BÁLDI and comprising the intertonguing "*Amussium Schlier*" and "*Glauconitic Sandstone*" sequences, form a depositional unit closely linked with the "*Budafok Formation with Anomia and larger Pectinids*" dated as Burdigalian already earlier and are to be referred to the newly established *Eggenburgian* (= Aquitanian + Burdigalian) *Stage;*
— the establishing of the Eggenburgian is justified not only by the fossil content of the strata belonging to it, but by the intensive post-Oligocene to pre-Miocene erosion as well.

The establishment of the Eggenburgian has led in Hungary to the logical solution of two problems:

(1) It has eliminated the controversy between the Hungarian (*i.e.* Upper Oligocene) and Slovak (*i. e.* Lower Miocene) interpretations of the "Chattian—Aquitanian" beds [*cf.* K. BALOGH et al. 1966. p. 26].
(2) It helped "find the coat that goes to the button to be sewed on": in other words, instead of knowning just the comparatively thin, *littoral* "Budafok Formation", now geologists have managed to recognize the respective *pelagic*, sublittoral sediments — the Amussium Schlier and the Glauconitic Sandstone.

CONSTRUCTIONAL PRINCIPLES

Most important of the above conclusions is for us to know that, as a result of the heavy denudation due to the Sava movements, the "Salgótarján Formation" lies for the most part immediately on the Rupelian "Kiscell Clay" or yet older formations [see *Fig. 2* in T. BÁLDI, 1969] rather than on the Upper Oligocene ("Egerian"). Between Šahy (Czechoslovakia), Balassagyarmat (Hungary) and Lučenec (Czechoslovakia) the basal members of the "Salgótarján Fomation" rest really on the crystalline schists of the Veporides; between Rimavská Sobota and Bretka (Czechoslovakia) and even at Alsószuha (Hungary) they lie on the Trias of the Southern Gemerides, while at Bušince (Czechoslovakia) they rest surely on the Kiscell Clay *(Fig. 2)*. The "Salgótarján Formation" is limited to the Cserhát, the northern foreland of the

ISOPACHYTE MAP OF THE OLIGOCENE SEDIMENTS IN NORTH HUNGARY

by

K. BALOGH

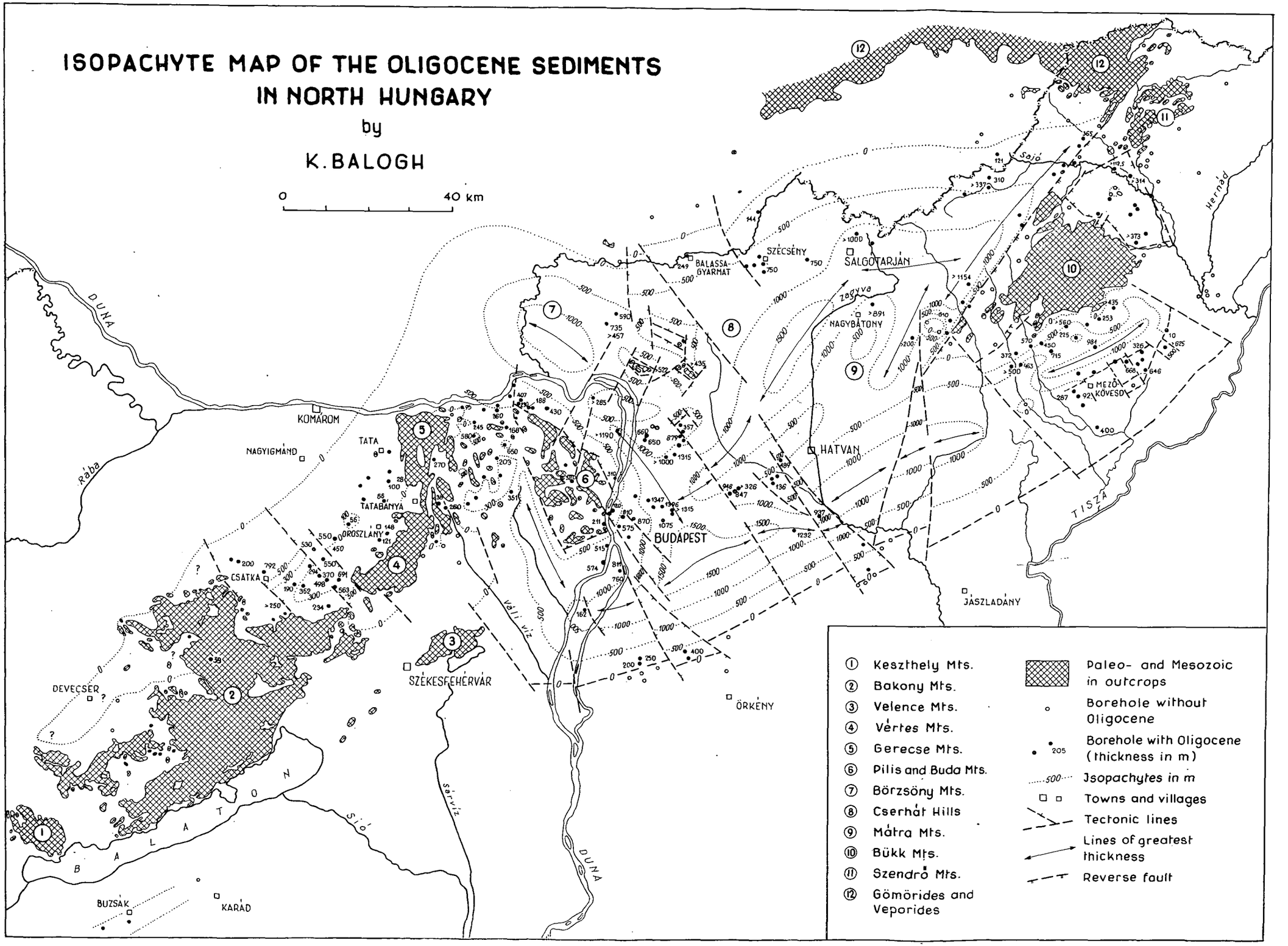

Fig. 3

Mátra and a part of the Borsod Basin. Accordingly, on the basis of the above, its sequence attaining even 800 m in thickness can be simply "peeled off" (with relatively little error) the Oligocene profiles, explored as they are *thus far* by drilling at Somoskőújfalu, Szécsény, Balassagyarmat, Sóshartyán, Nagybátony, Fedémes,

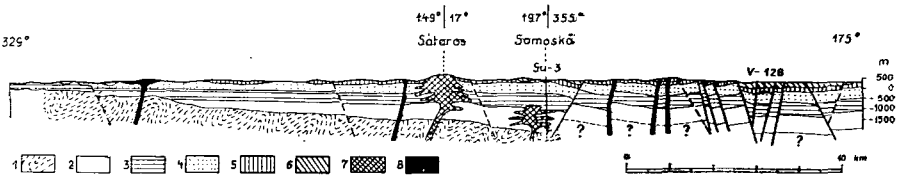

Fig. 2. The Rupelian transgression towards North. *1.* Paleozoic crystalline schists. *2.* Kiscell Clay (Rupelian). *3.* Amussium Schlier of the Salgótarján Formation. *4.* Glauconitic Sandstone of the Salgótartján Formation. *5.* Sandstone with Anomia and larger Pectinids. (*3—5.* Eggenburgian.) *6.* Coal-bearing beds of the Helvetian. *7.* Amphibole andesite subvolcanoes (Tortonian). *8.* Latest Pliocene basalte.

Ózd and Susa. Since there are no strata of such a controversial position anywhere else, a reduction like this need not be done for the lithological logs of boreholes drilled in other parts of the Oligocene basin. The cartographic representation of the total thicknesses, corrected or without correction, will then yield such a smallscale isopach map which provides a rather real portrayal of the contemporary vertical and lateral dimensions of the North-Hungarian—South Slovak Oligocene sequences — a general review consistent with the current stratigraphic conception *(Fig. 3).*

The mapped contours of the extension of the Oligocene, supposed or observed, have been controlled naturally by post-Oligocene tectonics and denudation. Hence they can be identified with the contemporaneous basin margins just in a few places. Particularly striking is the effect of post-Oligocene denudation on the NE and S borders of the Oligocene belt. Presently, this is the principal drawback to reconstructing the connections that existed between this belt and the other parts of the Paratethys.

Because of the uneven distribution of drilling data the thicknesses have had to be determined in many places by extrapolations relying upon the trends of increase or decrease, shown by the thickness of the sequence in the surroundings, as well as upon the general *gravitational* or *seismic* pattern of the region. Most of the hypothetical thickness data thus obtained coincide, of course, with the areas of greatest potential thicknesses. Nevertheless, on account of post-Oligocene tectonics and denudation as factors controlling the extension of the formation the areas of maximum thicknesses do not in all of the cases represent those basin portions which subsided at the highest rate. However, it can also be supposed that later tectonics happened to rejüvenate along "synsedimentary" foult-lines responsible for the most intensive subsidences. This is the reason why the authors has sought to adjust the strikes of the greatest thicknesses to the trends of tectonic lines borrowed from the general geologic maps of Hungary [K. BALOGH, L. KŐRÖSSY, 1966.] The rightness of this approach is proved by several examples substantiated by drilling logs:

(a) The greater thickness of the Oligocene beds of the Maklár Graben running on the S side of the Bükk Mountains, as compared to the figures observed in the vicinity, for instance, seems to be due to the pre-Miocene origin of the Graben.

Hence the unusually great thickness even of the Lower Miocene terrestrial sediments accumulated in this base level zone *(Fig. 4)*. On the other hand, on account of the deeper morphological position the Oligocene beds themselves have been preserved as shown by their profile which is more complete than to the N and S of the Graben.

(b) On the W border of the Bükk and Uppony Mountains the so-called Darnó Reverse Fault, accompanied in the west by a SSW—NNE trending gravimetric minimum, can be traced to run up to the Rudabánya Mountains. The minimum is seemingly due to local thickening of the Oligocene and Lower Miocene formations here, for on the E side of the Darnó Line the Oligocene is totally absent, the Lower Miocene being very limited in thickness. The situation is complicated by that the Darnó movement appears to have taken place on the very boundary between the rapidly — and slowly — subsiding parts of the Oligocene (and Lower Miocene) basin. Consequently, the thickening of the Oligocene here may also be indicative of a more rapid subsidence of the original sedimentary belt and of the rejuvenation of synsedimentary tectonics. Whichever be the case, the connection of the thickening of the sequence with the present-day pattern of the Darnó Reverse Fault is obvious.

(c) The thickness-controlling role of the tectonic lines is also evidenced by the comparatively dense drilling data of the piedmont basin portions of the Transdanubian Central Mountains.

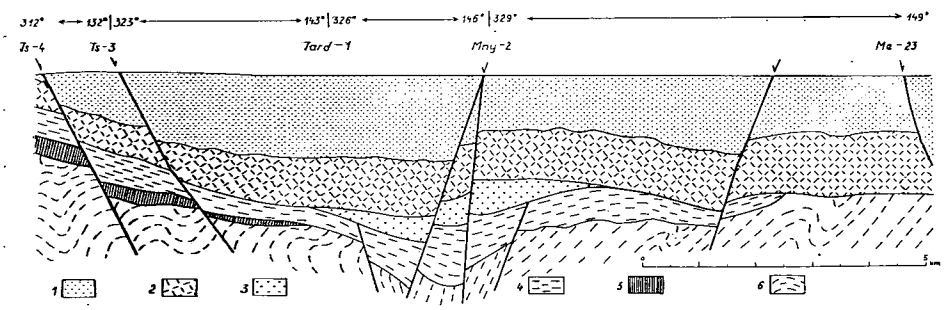

Fig. 4. Profile of the Maklár Graben. *1.* Pliocene. *2.* Miocene eruptive tuffs. *3.* Lower Miocene terrestrica. *4.* Oligocene. *5.* Eocene. *6.* Triassic.

In general, it can be observed that the major Mesozoic blocks are surrounded — after transitional zones of varying width — by zones of marked basement deepening showing greater, though varying, thicknesses of sediment. The opposite flank of these zones of subsidence is indicated by greater elevations of the basement and, correspondingly, by smaller total thicknesses of the Oligocene. On our map *(Fig. 3)* this observation has been extrapolated to the zones along the SE, N, NW and W borders of the North Hungarian Paleogene belt, so to the areas of Tököl and Kerecsend; Cinkota, Salgótarján and Fedémes; the central Börzsöny Mountains, and the Mány Basin, too. On the contrary, smaller thicknesses of sediment are shown to occur in the region of Tököl, Őrszentmiklós, Gödöllő—Tura (*observed* data) and beneath the Mátra Mountains (*extrapolated* data).

STRATIGRAPHY AND PALEOGEOGRAPHY

The present map will only become paleogeographically interpretable, when beside the isopach lines the geographic boundaries of the principal (marine, brackish and terrestrial) facies traversed by these lines are also indicated. Geohistorically, the main point is to know the relation of the Oligocene beds to the earlier members of the Paleogene. In this connection the following can be said.

The North Hungarian Paleogene includes two distinct subdivisions:

i. The lower member of maximum 350 to 400 m thickness, which ranges from the Sparnacian up to the uppermost Eocene, begins with terrestrial, fresh and brackish water deposits including brown-coal seams. These grade into a marine, warm-water limestone and marl sequence characterized by *Nummulitids* and *Discocyclines* suggesting Alpine and North Italian connections. This transgression must have been interrupted several times by ephemeral oscillations (as evidenced by further coal-seams). However, this has caused little change, if any, in the *predominantly calcareous type* of the sediments accumulated. Accordingly, the Paleocene-Eocene sequence, which is considered, with some simplification, to have the Bryozoan and the Buda Marls as its final member, is a very, for the most part calcareous, formation.* The inherent transgression progressed on the NW and SE sides of the Transdanubian Central Mountains in SW—NE direction, overriding, with angular unconformity, various Palaeo—Mesozoic horizons. It was not until the Middle Eocene that it reached the areas of the contemporary Danube Bend. The Bükk and the Rudabánya Mountains' territory was reached by it as late as the Upper Eocene. As for its basin, merely the W part of it is known with satisfactory precision. The line of maximum depth seems to have extended on the N side of the Transdanubian Central Mountains, letting coal-accumulating bays intrude into the depressions of varying size and kinetic machanism of the Central Mountains.

ii. A totally different pattern is exhibited by the *higher member* (spanning the entire Oligocene) of the North Hungarian Paleogene. Beside being 3 to 4 times as thick as the former, it is entirely *clastic* (conglomerates, sandstones, sands, sandy and clayey siltstones, and clays). Layers exceeding clay-marls in $CaCO_3$ content are very rare. However, interbedded andesite tuffs occur frequently. Most conspicuous of the changes in the fauna is the total decline of *Nummulites*. New paleogeographic connections were brought about, as evidenced by the admixture of boreal forms to the Mediterranean faunal elements.

In these changes the Latest Eocene emergence of the Transdanubian Central Mountains played a considerable role. Although in the NE part (region of Tokod and Esztergom, Pilis and W half of the Buda Mountains) of the Central Mountains this movement was of short duration, the depressions which had been carved out by erosion were covered by a variety of terrestrial sediments. However, the basin portions at Héreg, Gyermely, Szomor, Mány and Zsámbék and the territory of the basins between the Bakony, Vértes and Gerecse remained emergent till Late Oligocene time, the Bakony territory was dry land during the whole Oligocene. The emergence largely reduced the connections with the SW which had existed here throughout the Eocene epoch. Accordingly, the only marine connection that may be supposed to have existed in the afore-mentioned direction seems to have been to the S of Lake

* Newest references to the problem of the Eocene-Oligocene boundary are: M. BÁLDI BEKE, 1970, E. DUDICH, JR.—L. GIDAY, 1969, Á. JÁMBOR et al., 1966, G. KOPEK, 1969, A. ONDREJIČKOVÁ—J. SENEŠ, 1965, J. SENEŠ, 1964, E. SZŐTS, 1961, 1968.

Balaton, as suggested by the Lower and Middle Eocene deposits uncovered by drilling at Karád and Buzsák.

So the wide and long sea branch which had crossed Hungary in Late Eocene time, shrank into an ill-aërated brackish-water inland sea by the beginning of the Oligocene: a sea basin which did not grow wider until the advent of Middle and Late Oligocene transgression which progressed partly westwards and partly northwards *(Fig. 5)*. Geohistorically, the resulting North Hungarian Paleogene basin can be

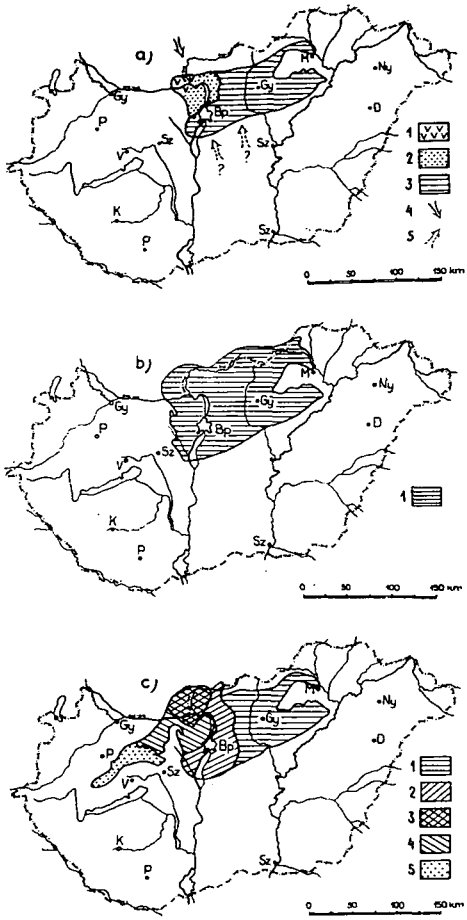

Fig. 5. Paleogeographical sketches of North Hungary in the Lower *(a)*, Middle *(b)* and Upper Oligocene *(c)*.

a) *1.* "Hárshegy Sandstone" in fluviolimnic facies, covered with brackish "Lower Cyrena Beds". *2.* "Hárshegy Sandstone" with marine intercalations, without Cyrena beds. *3.* The euxine "Tard Clay" facies. *4.* River-course. *5.* Assumed river-course.

b) *1.* Pelagic "Kiscell Clay".

c) *1.* "Eger Formation" (deep-littoral to littoral—lagoonal beds). *2.* "Törökbálint Formation" (Schlier to shallow-sublittoral Pectunculus-sands). *3.* "Esztergom Formation" (regressive, then marine beds, covered with alternation of Pectunculus- and Cyrena-beds. *4.* "Mány Formation" (predominante Cyrena-beds, poorly intercalated with Pectunculus-beds. *5.* "Mór Formation" (deltaic facies, in W more terrestrical).

divided into the following four main subdivisions progressing from the NE to the SW *(Fig. 6)*.

(a) The eastern main basin now traceable (because of later denudation) from the SE part of the Buda Mountains only to the Bódva—Sajó line. Its depression is filled up by a complete Oligocene sequence joining the Upper Eocene *without any break in sedimentation (Fig. 6: a)*.

b) The Danube Bend part of the Hungarian—North Slovak area, where the complete Oligocene sequence beginning with deltaic sediments is separated from the Eocene by a *short hiatus (Fig. 6: b)*.

c) The basin portions lying on the E and W sides of the Gerecse and extending from there up to the NE border of the Bakony Mesozoic — areas that were reached only by the *Upper Oligocene transgression* decayed towards W *(Fig. 6: c)*.

d) The Bakony Mountains and their immediate foreland characterized by purely terrestrial sedimentation *(Fig. 6: d)*.

Ad a) The Oligocene sequence of the eastern main basin represents essentially one cycle of sedimentation.

The *lowermost member* is constituted by 40—80—130 m of *Tard Clay-Marl* — a formation abunding in bacteriopyrite, bitumen, and plant and fish remains referring to Euxine conditons. Despite the continuity of sedimetation, it shows definitely regressive features as compared to the final Eocene beds rich in Foraminifera and

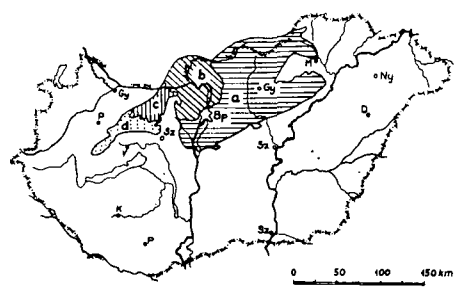

Fig. 6. Subdivision of the North Hungarian Oligocene Basin. *a)* The Eastern Main Basin. *b)* The NW margine of the Eastern Main Basin. *c)* The western regions submerged only in the Upper Oligocene. *d)* The foreland of the Bakony Mountains with terrestrical sediments.

other marine fossils. This observation is corroborated by its alternation with sandstones and andesite tuffs and laminae resembling menilitic shales; by the lack of Foraminifera in it and by the limitation of its *Mollusc* fauna to a few brackish-water species *(Cardium lipoldi* ROLLE*)*.

The *transgressive branch of the cycle* is represented by the 400- to 1100-m-thick sequence of the *Kiscell Clay* developing gradually from the Tard Clay-Marl. In its fauna — beside thin-shelled *Bivalves* and *Gastropods* and mud-eating sea urchins — the representatives of *Foraminifera* are predominant. On the basis of the last-mentioned fossils the formation can be split up into a number of local horizons, for the most part of local significance. *Clavulinoides szabói* (HANTKEN), the index-fossil of the formation, is present in all of the horizons.

Although interbedded sandstones of varying thickness and grain size increasing towards the basin margins and andesite tuff layers are not absent in the Kiscell Clay either, this formation is considered on the whole to have been deposited in a pelagic,

neritic to bathyal environment. In accordance with its transgressive character, the clay is of larger extension as compared to the Tard beds underneath. Its northward expansion is clearly observable in the vicinity of Szécsény, Balassagyarmat (Hungary) and Bušince (South Slovakia). In the last two localities its strata correlated with the higher levels of the Kiscell Clay rest, with their 40 to 50 m of basal sands and gravels, directly on the crystalline schists of Vepor type [V. HOMOLA, 1958, K. SLAVÍKOVÁ, 1958, K. BALOGH *et al.*, 1966]. It is, however, a debatable point whether this unfossiliferous, gravelly, basal formation may replace *only* the deeper part of the Kiscell Clay, or it may correspond to both the Kiscell Clay and the Tard Clay-Marl combined? The superposition of the Kiscell Clay to the crystalline basement is nevertheless a clear testimony to transgression *(Fig. 2)*.

The *regressive branch of the cycle* is represented by the Upper Oligocene sequence becoming upwards gradually sandier. Its 180-m-thick profile uncovered in WIND's clay pit at Eger and in its footwall (by drilling), contains the richest Upper Oligocene fauna of the Central Paratethys. On account of its having been exhaustively studied [T. BÁLDI, 1966] the Eger Formation has become the stratotype of the central Paratethyan Upper Oligocene, despite the fact that pre-Miocene denudation had removed about 50 m of sediment with similar fauna from the top of the Eger type-section, as suggested by a comparison with other profiles. Above the Upper Oligocene glauconitic-tuffitic sandstone sequence, developing gradually from the Kiscell Clay, the formation comprises deep-littoral molluscan clays (bottom) and an alternation of shallow-littoral sands and clays (top). The sequence ends with littoral-lagoonal gravels and coarse-grained sands including layers with *Cyrena, Mytilus, Cerithium* and *fossil plant remains.* Consequently, regression is paleontologically proven, too.

As for the western margin of the main basin (SE half of the Buda Mountains, Pest Plain), its geohistorical evolution differs from the above only by that the Upper Oligocene sequence is of „Törökbálint" (or „Kováčov") — but not of "Eger"—type. Accordingly, the Lower Oligocene, lying above the "Buda Marl" which on the basis of *Nannoconus* [M. BÁLDI-BEKE, 1970] can still be referred to the Upper Oligocene, is represented here too by a typical "Tard Clay", and the Middle Ogilocene is by a typical "Kiscell Clay". The Upper Oligocene regression, however, is here less acute than it is in the east, for it has come only to the sedimentation of *shallow-sublittoral* beds ["Pectunculus" or, more properly, "Glycymeris Sands"], wich overly — at Kováčov (Czechoslovakia) immediately, at Törökbálint (Hungary) through the interposition of a schlier facies — the pelagical "Kiscell Clay" ("Kováčov Formation" or "Törökbálint Formation", respectively, T. BÁLDI, 1969).

The most marine sequence of the Oligocene thus occurs on the eastern slope of the Buda Mountains. This fact is particularly conspicuous, since the marine sedimentation observable in the east grades into purely continental one in the west. Let us review the various stages of this development in the following.

Ad b) To the west, first of all a transitional zone is found, which can be delineated by the Nyergesújfalu—Tát—Nagysáp—Dág—Biatorbágy line and includes the region of Dorog, Esztergom, Šturovo and Kovačov as well as the Triassic blocks on the Hungarian side of the Danube — the Pilis and the western part of the Buda Mountains. This belt is always devoid of the two final members of the Upper Eocene: the Bryozoan and Buda Marls. The more so, the Oligocene rests directly on the Trias in many places: a manifestation of the higher intensity of "infra-Oligocene denudation". Its sequence begins with an average of 50 to 80 m of coarse-detrital "Hárshegy Sand-

stone" which was observed in several places intertonguing with the "Tard Clay" of the eastern basin.

In the vicinity of Dorog, Esztergom and Šturovo the Hárshegy sandstone is comparatively thin (a max. of 20 to 25 m, if present at all) and of definitively continental (fluviolimnic) origin. They are overlain here by 50 m of what is called "the Lower Cyrena Clay" whose deposition in a water environment of limited salinity (increasing upwards nevertheless) is evidenced beside the presence of brown-coal stringers by its fauna indicative of a Lower Oligocene age [Z. SIPOSS, 1964, A. ONDREJIČKOVÁ, J. SENEŠ, 1965, J. SENEŠ, 1964].

In the blocks occurring on the Hungarian side of the Danube the thickness of the Hárshegy Sandstone increases to 150 m, whilst the "Lower Cyrena Clay" is absent. The sandstone overlies the Upper Eocene through the intermediary of shaly clays of Tard facies. Whereas its deeper member is terminated by refractory clays with brown-coal stringers (*i. e.* a limnic facies), the higher member was found to include *Ostrea-* and *Pecten*-bearing intercalations, *i. e.* layers of marine character. However, intercalations of this kind have also been shown to occur in the Hárshegy Sandstone of the Pilis and Buda Mountains as well [E. VADÁSZ, 1960].

On the strength of its features and limited extent the Hárshegy Sandstone may be considered with conviction to represent deltaic deposits of a short, but steeply sloping, river (or river system) that came to enter the Oligocene basin from the direction of the crystalline masses of the Western Carpathians.* Consequently, it is not an abrasional detritus originating from high river banks, but it is constituted by river-transported gravels and sands which were distributed — at least locally — by sea water movement. Their conditions of deposition varied with the different stages of development of the delta, showing the following facies: river-channel and flood-plain, limnic, lagoonal, brackishwater and littoral. Whereas in the quiet bays on the west flank of the delta coal formation was coupled with accumulation of comparatively fine detritus, the coarse detrital material of some branches of the delta penetrated astonishingly far into the eastern basin centre characterized by the Tard facies (see the „Hárshegy Sandstone" which is 63-m-thick in the borehole Csepel-2 and 130-m-thick in Tóalmás-2).

In the Middle Oligocene, transgression continued here, too. However, in accordance with the basin-marginal position of the area, its sequence begins with sediments coarser than the Kiscell Clay (the "*lower transgressional sandstone*" of J. SENEŠ, 1964 a and b), and the "*foraminiferal clay facies*" follows only above this.

The *Upper Oligocene* is characterized by a great variety of facies. For example, in the vicinity of Esztergom and Štúrovo, it seems to form an independent cycle that can be called *Esztergom Formation.* The shallowing of the sea is manifested by the "*Upper Sandstone Beds*" of Štúrovo, respectively of the borehole Solymár-72., in the hanging wall of the Kiscell Clay. These beds are followed here by the deposition of purely marine sediment. This ephemeral transgression, however, which seems to be connected with the inundation of the basins of the Gerecse region in Late Oligocene time, leaded finally into an oscillatory (thus, taking the *entire* sequence in considera-

* So far not too many objections to the inclusion of the Hárshegy Sandstone in the Lower Oligocene have been raised. It is plausible, however, that the formation of a few isolated, continental (hence unfossiliferous) occurrences began as early as the Upper Eocene — a hypothesis seemingly supported by the absence of the Hárshegy Sandstone above the Buda Marl throughout the occurrences of this latter. Accordingly, the deepest member of the Hárshegy Sandstone would replace the Buda Marl, while its bulk would be equivalent to the Tard Clay-Marl.

tion: regressive) phase. This phase is characterized by the frequent alternation of shallow-sublittoral "Pectunculus-beds" with brackish-water "Cyrena-deposits".

In other points of the parts of the Pilis and Buda Mountains belonging here, the whole Upper Oligocene is filled up by an oscillatory sequence varying among littoral, brackish-water and even terrestrial facies.

Ad c) Particularly enough, it is this oscillatory Upper Oligocene, with the total absence of the Lower and Middle Oligocene, that transgresses farther west in the basins around the Gerecse Mountains. According to T. BÁLDI [1965, 1967], in the Mány—Zsámbék basin the transgressive character would gradually wane from the E to the W, because in the oscillatory sequence, with the progressive decrease in the number of shallow-sublittoral intercalations, it is the brackish-water deposits that will predominate, being associated with freshwater layers. This "*Mány Formation*" of brackish-water predominance has periodically penetrated into the freshwater Tatabánya—Csatka Basin (formed simultaneously on the N side of the Vértes) across the internal (Héreg, Tardos and Tarján) basins of the Gerecse.

Ad d) The bulk of the Upper Oligocene Tatabánya—Csatka Basin, and particularly its borders facing the Vértes and Bakony Mesozoic, are constituted, however, for the most part, by the "*Mór Formation*" of terrestrial-limnic type. Beginning with variegated clays and coarse basal detritus, the sequence of this formation locally contains coal stringers and even minor brown-coal seams (already stripped off): in the vicinity of Vértessomlyó, Bakonycsernye, Jásd and Szápár. Now filled up by sediments of 500 to 800 m thickness, the basin was joined in the west by a river delta. In these deltaic sediments accumulated in the territory of the Northern Bakony Mountains the ratio of the fine-grained rocks increases from the Hárskút—Zirc—Bakonycsernye—Bakonyszentkirály area towards the Réde—Csatka—Nagyveleg—Mór zone, while the variety of gravels decreases [J. KNAUER, 1969]. Accordingly, the trends of distribution of the facies here are the same as in the marine-brackish facies of the Upper Oligocene.

The outlined distribution of the facies and geohistorical characteristics of the North Hungarian—South Slovak Oligocene indicates at the same time the potential occurrences of associated mineral raw materials (deposits).

Oil and gas reservoirs, for instance, are expected to occur in the eastern basin only. This conclusion can be motivated by the following considerations:

i. The bituminous Tard Clay, which may have served as mother rock, could develop only there where sedimentation on the Eocene—Oligocene boundary was not interrupted, but continued under euxinic conditions.

ii. Here the Tard Clay is overlain by a Middle Oligocene so thick that it must contain several layers capable of trapping hydrocarbons enclosed in impervious clays or clay-marls.

Brown-coal deposits workable from both quantitative and qualitative points of view can only be found, however, in the western basin portions and always at the base of those marine, brackish or freshwater sequences whose deposition was preceded by a shorter or longer infra-Oligocene denudation. There were possibilities for deposition of coal in thinner lentils or beds in two instances and two different places:

i. in the Lower Oligocene on the west flank of the Hárshegy Sandstone delta (vicinity of Esztergom—Šturovo);

ii. in connection with the Late Oligocene shallowing of the basin (Šturovo) and

transgression in the marginal parts of the Tatabánya—Csatka Basin (Vértessomlyó, Szápár, Jásd, Bakonycsernye).

The thicker portions of the layers are already falled. The economical value of the rest has no importance.

REFERENCES

BALOGH, K. et al. [1966]: Magyarázó Magyarország 200 000-es földtani térképsorozatához. M-34-XXXII. Salgótarján. — Budapest, pp. 21—38.

BALOGH, K., KŐRÖSSY, L. [1968]: Tektonische Karte Ungarns im Maßstabe 1:1 000 000. — Acta Geol. Acad. Sci. Hung., **12**, pp. 255—262.

BALOGH, K., RÓNAI, A. [1965]: Magyarázó Magyarország 200 000-es töldtani térképsorozatához. L-34-III. Eger. — Budapest, pp. 32—43.

BÁLDI, T. [1965]: A felsőoligocén pektunkuluszos és cyrenás rétegek települési és ősföldrajzi viszonyai a Dunazug hegységben. (The stratigraphic and paleogeographic relations of the Upper Oligocene Pectunculus- and Cyrena-beds in the Dunazug Mountains. — in Hungarian, with English resume) — Földt. Közl., **95**, pp. 423—436.

BÁLDI, T. [1966]: Az egri felsőoligocén rétegsor és molluszkafauna újravizsgálata. (Revision of the Upper Oligocene Molluscan Fauna of Eger (N-Hungary). — in Hungarian, with English resume) — Földtani Közlöny **96**, pp. 171—194.

BÁLDI, T. [1967*a*]: A Mány—Zsámbéki-medence felsőoligocén makrofaunája. (Oberoligozäne Makrofauna des Beckens von Mány—Zsámbék. — in Hungarian, with German resume) — — Földt. Közl., **97**, pp. 436—446.

BÁLDI, T. [1967*b*]: A magyarországi felsőoligocén molluszkafauna. — (Manuscript, only in Hungarian).

BÁLDI, T. [1968]: Az európai neogén emeletek helyzetéről. — Földt. Közl., **98**, pp. 285—289.

BÁLDI, T. [1969]: Le Miocène inférieur de Hongrie. — Colloque sur la Néogène. Budapest, 4—8 Septembre. Matériaux des séances plénaires et section. — Réunion organisée par la Société Géol. de Hongrie à l'occasion du centennaire de l'Institut Géol. de Hongrie. pp. 7—24.

BÁLDI, T., HÁMOR, G., JÁMBOR, Á., KÓKAY, J. [1969]: Földtani kirándulások magyarországi neogén területeken. — A MÁFI centenáriumának tiszteletére rendezett Neogén Kollokvium kirándulásvezetője. 1969. IX. 5—8. pp. 20—25. és 29—30.

BÁLDI, T., RADÓCZ, GY. [1969]: Stratigraphy of the Egerian and Eggenburgian Formations between Bretka and Eger (NE-Hungary). — Colloque sur la Néogene. Budapest, 4—8 Septembre. — Matériaux des séances plénaires et section. pp. 15—34,

BÁLDI-BEKE, M. [1970]: A bryozoás és budai márga nannoplankton faunája. (The Nannoplancton of the Bryozoan and Buda Marls [Paleogene of Budapest, Hungary]. — in Hungarian, with English resume) — Őslénytani Viták **16**, pp. 31—49.

CSIKY, G. [1956]: A Budapest környéki újabb szénhidrogénkutatások és azok földtani eredményei. (The latest prospecting activities for oil and gas in the vicinity of Budapest and their geological results. — in Hungarian, with English resume) — Földt. Közl., **86**, pp. 373—389.

CSIKY, G. [1961]: Az észak-magyarországi szénhidrogén kutatások kőolajföldtani eredményei. (Oil geological results of prospecting for oil and gas in North Hungary. — in Hungarian, with English resume) — Földt. Közl., **91**, pp. 95—120.

CSIKY, G. [1968]: A szénhidrogénkutatások újabb eredményei és kilátásai az északi paleogén-medencében. (Latest results and perspectives of hydrocarbon prospecting in the northern Paleogene basin of Hungary. — in Hungarian, with English resume) — Földt. Közl., **98**, pp. 29—40.

CSONGRÁDI B. MRS., KŐVÁRY, J., MAJZON, L. [1959]: Adatok a Budapest környéki medencerészek rétegsorához. (Contributions to the stratigraphy of the basins around Budapest. — in Hungarian, with English resume) — Földt. Közl., **89**, pp. 407—412.

DUDICH, E. JR. [1959]: Paläogeographische und paläobiologische Verhältnisse der Budapester Umgebung im Obereozän und Unteroligozän. — Ann. Univ. Sci. Budapestinensis de R. Eötvös Nom. — Sect. Geol., **2**, pp. 53—87.

DUDICH, E. JR., GIDAI, L. [1969]: Intervention concernant la limite Éocène/Oligocène. — Mém. BRGM. **69**, Coll. sur l'Éocene **3**, pp. 444—445. Paris.

GIDAI, L. [1970]: Az eocén képződmények rétegtani helyzete a Dunántúli Középhegység ÉK-i részén. (Stratigraphische Stellung der Eozänablagerungen im Nordostteil des Transdanubischen Mittelgebirges. — in Hungarian, with German resume) — Földt. Közl., **100**, pp. 143—149.

HOMOLA, V. [1958]: Lithologický a stratigrafický profil opěrné vrtby (Bušince 1). Práce Ústavu pro naft. výzkum. **10.** 41. pp. 23—26.

JÁMBOR, Á. *et al.* [1966]: Magyarázó Magyarország 200 000-es földtani térképsorozatához. L-34-II. Budapest. — pp. 42—70.

KNAUER, J. [1969]: Bakonyi földtani munkánk néhány eredményéről. — Relat. ann. Inst. Geol. Publ. Hung., 1967. pp. 29—33.

KOPEK, G. [1969*a*]: Az ÉK-i Bakony és a Vértes Ny-i előterében folyó kőszénkutatás 1967. évi eredményei. (Les résultats de la prospection de lignite dans la région nord-est de la Montagne du Bakony et dans l'avantpays de l'ouest de la Montagne Vértes obtenus en 1967. — in Hungarian, with French resume) — Relat. ann. Inst. Geol. Publ. Hung., 1967, pp. 58—72.

KOPEK, G. [1969*b*]: Összefüggések a távlati kőszénkutatás és a Dunántúli-Középhegység eocénjének faciológiai és fejlődéstörténeti kérdései között. (Relations entre la prospection de lignite perspective et les questions de l'évolution géologique et de la faciologie de l'Éocène du Montagne Centrale de Transdanubie. — in Hungarian, with French resume) — Relat. ann. Inst. Geol. Publ. Hung., 1967, pp. 45—54.

KOPEK, G., KECSKEMÉTI, T., DUDICH, E. JR. [1965]: Stratigraphische Probleme des Eozäns im Transdanubischen Mittelgebirge Ungarns. — Acta Geol. Acad. Sci. Hung., **9**, pp. 411—426.

KŐRÖSSY, L. [1970]: Entwicklungsgeschichte der neogenen Becken in Ungarn. — Acta Geol. Ac. Sci. Hung. — **14**, pp. 421—429.

ONDREJIČKOVÁ, A., SENEŠ, J. [1965]: Oligocén južného Slovenska a jeho mäkkýsová fauna. (Das Oligozän der Südslowakei und seine Molluskenfauna. — in Slovakian, with German resume) — Sborník Geol. Vied. Západné Karpaty **4**, pp. 145—198.

RADÓCZ, GY. [1969]: Előzetes jelentés a csereháti alapfúrások eredményeiről. (Vorläufiger Bericht über die Ergebnisse der Csereháter Basisbohrungen. — in Hungarian, with German resume) — Rel. ann. Inst. Geol. Publ. Hung., **1967**, pp. 281—285.

SENEŠ, J. [1964*a*]: Az üledékképződéssel egyidejű kéregmozgások időbeli helyzete a szedimentációs ciklusokban. — Földtani Kutatás **7**, 2—3. pp. 36—41.

SENEŠ, J. [1964*b*]: A Štúrovo—Dorog—Tokodi alsó-oligocén problémái. — Földtani Kutatás **7**, 2—3. pp. 31—36.

SIPOS, Z. [1964]: Adatok az Esztergom-vidéki oligocén képződmények fáciesviszonyaihoz. (Contribution to the knowledge of the facies conditions of the Oligocene in the surroundings of Esztergom, Hungary. — in Hungarian, with English resume) — Földt. Közl., **94**, pp. 206—212.

SLAVÍKOVÁ, K. [1958]: Mikrofauna oligocenních sedimentu opěrné vrtby (Bušince 1). — Práce Ustavu pro naft. vyzkum. **10**, 41. pp. 27—34.

SZŐTS, E. [1961]: Rémarques sur les niveaux à Foraminifère du Paléogène en Hongrie. — Compt. Rend. somm. séances Soc. Géol. France **6**, Paris, pp. 161—162.

SZŐTS, E. [1968]: A budai „briozoumos—ortofragminás márga" és a tulajdonképpeni budai márga plankton Foraminiferáiról és rétegtani helyzetükről. (Les Foraminifères planctoniques de „la marne a Bryozoaires et Orthophragmines" et de la marne de Buda s. s., (Ofner Mergel s. s.) et leur position stratigraphique. — in Hungarian, with French summary) — Földt. Közlöny **98**, pp. 260—281.

TÁVLATI FÖLDTANI KUTATÁS [1963, 1964, 1965, 1966 és 1967]. — Edition of the Hungarian Geol. Institute, Budapest.

VADÁSZ, E. [1960]: Magyarország földtana. — Budapest. pp. 207—208, 213—240, 322—327.

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MINERAL SEQUENCE ON SOME Pb + Zn ORE DEPOSITS OF TURKEY

J. H. BERNARD

ABSTRACT

The paper contains a description of mutual sequence relations among the main minerals on some Turkish lead-zinc deposits, based on megascopic and microscopic observation of samples. The described deposits are ordered in the sense of the author's paragenetic classification as mineral associations A to G. Following localities have been studied: Murgul, Nefsishakköy, Kirnoba, Şihman-Mercan, Aksu near Muradin, Ağizlar, Harami, Kurnaköy, Muradin (Sisorta), Su Alti near Muradin, Çakiroba, Altinoluk, Kerakoca, Keban Maden, and Sarikeler Ocağı near Pozanti. Some more complicated mineral sequence schemas are shown also in the Tables from I to V.

During the period 1968—1970, the author has visited numerous polymetallic deposits in Turkey collecting the samples for his paragenetic research of isogenetic Pb + Zn mineral associations incl. the geochemical character of galena, sphalerite and tetrahedrite [1]. The amount of samples of some deposits allowed him to study also the mineral sequence. The result of the research based on a combination of the megascopic observation of handspecimens and of the microscopic study is submitted in the present paper.

When compared with some older data concerning the mineral sequence in the corresponding deposits, the author found often numerous generations of the common minerals such as quartz, pyrite, hematite, and even chalcopyrite. This characteristic feature is typical for almost all subvolcanic deposits not only in Turkey but is valid generally. On the other hand, the worker is aware that some accessory minerals lacking in his mineral sequence tables could be found after a longer research on deposits but cannot change the general character of the tables.

The studied localities are ordered in the sense of the paragenetic system of Turkish Pb + Zn deposits by BERNARD [1].

Association A — pyrite + Cu + Zn ± Pb association of stockworks and of younger epigenetic mineralizations on volcano-sedimentary or hydrothermal-sedimentary pyrite deposits, bound on Upper Cretaceous to Early Tertiary dacito-rhyodacite volcanism, in the northern zone of the eastern Pontids.

Murgul, Artvin vilayet

The ores are deposited in intensively altered dacites or rhyodacites* and tuffs in the form of stockworks composed of veinlets, silica rich impregnations and irregular mass. Main ore components are pyrite and chalcopyrite, the FeS_2: Cu ratio is, however, here much more favorable then on Cu poor pyrite deposits of the Lahanos type. Pyrite is present in numerous generations, represented mainly by strikingly

* Oral communication of. Ing. R. STOJANOV, Skopje.

big crystals (up to 3 cm) in form of combination of pentagonal dodekahedrons with the octahedron or even pure octahedron crystals belonging to the oldest generation. Chalcopyrite is mostly present in the form of impregnations and irregular mass; sphalerite forms veinlets (maximally 3—4 cm thick) often impregnated by chalcopyrite. Megascopically its colour seems to be black but in smaller grains a dark green-brown colour is visible. In cavities fine crystals of tetrahedral or triakistetra-

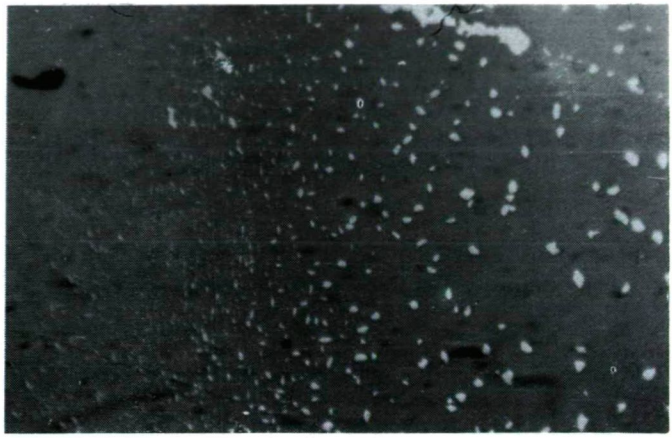
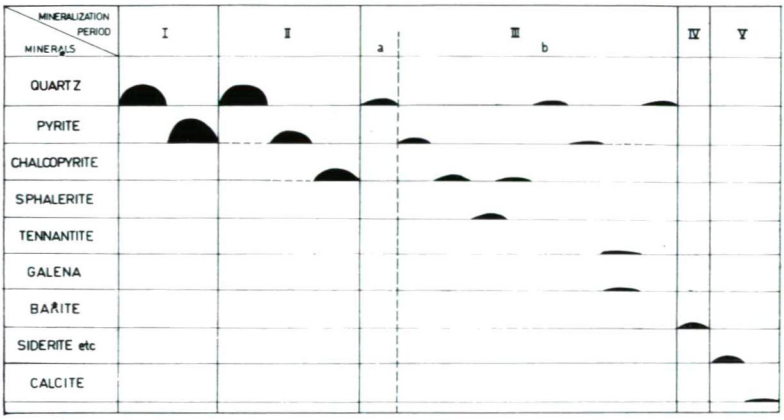


Fig. 1. Ex-solution structure of chalcopyrite in sphalerite from Murgul, Artvin vilayet. Magn. 160 x

hedral type can often be found. Galena is mostly found in impregnation as granular aggregate, tennantite (with predominance of As over Sb) and bornite form thin veinlets or massive aggregates in the altered country rock. Quartz (often as amethyst), barite and carbonates form crystalline aggregates, in cavities often very fine crystals of common habit are found.

TABLE I.



Mineral sequence on the ore deposit Murgul, Artvin vilayet

Mineral sequence:

WIJKERSLOOTH [8] published the following mineral sequence:

1st phase: magnetite (hematite)-pyrite-chalcopyrite-quartz,

2nd phase: chalcopyrite-bornite-sphalerite-galena-quartz,

3rd phase: tetrahedrite-yellow brown sphalerite-ankerite-barite.

Later SCHNEIDERHÖHN [7] described a simple sequence schema: pseudomorphous quartz + pyrite; clear quartz + chalcopyrite, galena, tetrahedrite, sphalerite, pyrite; clear quartz + hematite.

According to my field and microscopic research, the following sequence of main mineral components of the deposit was esteblished (Table 1):

1st mineralization period: The oldest hydrothermal component is represented by a mass of fine-grained quartz *I* impregnating altered country rocks and containing big crystals of pyrite *I*; pyrite crystals are often weathered out of the rock. The best locality for such pyrite crystals is in the upper level of the western section of the open mine (situation as of Summer 1969). Quartz *I* mainly of the upper zone is often formed as brick-red fine-grained variety pigmented by hematite and described as carneol [7].

2nd mineralization period: After intensive tectonic movements causing the brecciation of the altered country rock and minerals of the 1st mineralization period, a new portion of hydrothermal solution has ascended and has given the origin of quartz *II* with some ores. This mostly colourless or white crystalline or crystallized quartz contains the pyrite *II* in form of small irregular grains or crystals and the main mass of chalcopyrite. The mineralization of the both early periods represents the absolute majority of all hydrothermal products on the deposit.

3rd mineralization period: Locally in cavities, the radiated aggregates of quartz *III* (amethyst) have crystallized. This striking vein filling is afterwards cut by veinlet system of younger minerals. Among them the oldest is pyrite *III* as fine-grained aggregate, then chalcopyrite *II* in big grains and massive textures. It is often associated with granular sphalerite containing another chalcopyrite generation *(III)* as very fine-grained oriented inclusions representing a product of a complex solution; they can be even partly interpreted as real ex-solutions from the solid solution $ZnS - CuFeS_2$.

Quartz *IV* as the next member of the sequence is only in microscopic amounts. It forms metacrysts on boundaries between sphalerite and chalcopyrite *III*. Younger is pyrite *IV* as groups of grains of crystals cutting the mass of sphalerite and crystals of quartz *IV*. The next minerals are tennantite and galena the mutual sequence position of which cannot be determined due to their non-simultaneous occurrence. Galena forms granular filling of veinlets cutting sphalerite and older minerals. Tennantite found even in bigger mass is mostly fine-grained and penetrates the sulphidic filling; its relation to pyrite *IV* is unknown. In cavities and druses the crystals of previously described sulfides are covered by small druse of colourless quartz *V*.

4th mineralization period: Monomineral barite mineralization cuts all previous hydrothermal products in veinlets or forms very fine tabular crystals up to 3 cm big in cavities.

5th mineralization period: This period has an almost carbonatic character. It is represented mainly by siderite as granular aggregate in veinlets or, in cavities, as fine lenticular crystals often covered by younger white columnar crystals of calcite. Less common is ankerite and dolomite which form young filling together with siderite or a cement in the breccia with fragments of older minerals incl. barite.

Later the secondary minerals such as limonite, Cu-carbonates etc. originated. Many other rarer minerals can be expected on the deposit but their discovery needs more detailed field research.

From the neighbouring deposit *Kuvarshane, Artvin vilayet,* WIJKERSLOOTH [8] has described the mineralization in three periods (phases):

1st period — quartz, pyrite and chalcopyrite (+ some sphalerite),

2nd period of polymetallic character with younger generation of chalcopyrite,

3rd period — calcite.

According to my observation also tennantite and barite are the characteristic accessories in Kuvarshane.

Nefsishakköy (Batlama), Giresun vilayet

In the studied material the main components are black sphalerite and chalcopyrite with some pyrite and a microscopic amount of tennantite and barite. Quartz is the main gangue mineral. All named minerals cement fragments of the altered dacitic country rock.

Sphalerite seems to be here the oldest of observed sulfides. It is penetrated by other named minerals in veinlets or groups of grains in the following sequence: quartz—pyrite—chalcopyrite—tennantite.

Association B — Pb + Zn + Cu association of ore veins in the effusive rocks and tuffs bound on plutonic and subvolcanic magmatism in the northern zone of the eastern Pontids.

Kirnoba, Gümüshane vilayet

The samples show complicated textures, mainly with ore minerals. The mineral sequence is as follows:

1st mineralization period: As the oldest mineral has been determined the quartz *I* in fine-grained aggregate penetrating the country rock.

2nd mineralization period: The main ore filling is formed by brown sphalerite aggregate; on its surface in cavities and even on walls of the partly brecciated sphalerite aggregate sit many pentagonal-dodekahedral crystals and grains of pyrite *I* forming often bigger accumulations in ore veins.

3rd mineralization period: This is the main ore period. After an intensive brecciation of the older mass, tetrahedrite (with dominance of Sb over As) cemented the breccia so that the fragments of sphalerite and pyrite *I* seem to flow in tetrahedrite. Chalcopyrite in small amount penetrates in veinlets the mass and is younger than tetrahedrite. Later, after another brecciation, quartz *II* with very fine-grained pyrite cement the older mass, the quartz *II* often forming fine metacrysts towards the older sulfides. The last important ore mineral is the granular galena.

4th mineralization period: After a brecciation a coarse—grained barite aggregate of brown-yellowish colour penetrates the mass.

5th mineralization period: Cutting all previous ore vein fillings, ankerite is the last primary mineral.

KIEFT [4] found here the following sequence: pyrite—sphalerite—chalcopyrite and tetrahedrite—galena.

Sihman—Mercan, Ordu vilayet

Intensively whitened andesite and tuffs are penetrated by a system of veins formed by light grey quartz containing big grains of galena, green-brown sphalerite, chalcopyrite, and pyrite. The sulphides sequence is as follows: pyrite — chalcopyrite *I* in massive aggregates — sphalerite with chalcopyrite *II* inclusions — galena.

Afterwards was the sulfide filling brecciated and cemented by very abundant druse of younger white quartz *II* with numerous crystals. The last hypogene mineral is the brown ankerite in crystals covering quartz *II* crystals in cavities.

Aksu near Muradin, Ordu vilayet

Galena, dark yellow-green sphalerite and some chalcopyrite form big metacrysts in a fine-grained calcite-dolomite aggregate of hydrothermal origin cementing altered clastic effusive country rock. Younger ankerite in veinlets with common druse cuts and the partly brecciated sulphides.

Ağizlar, Gölköy ilce, Ordu vilayet

Altered andesite contains narrow ore veins with polymetallic mineralization formed mainly by quartz and sulphides. A yellow-green or yellow-brown sphalerite predominates together with galena. The general mineral sequence is as follows:

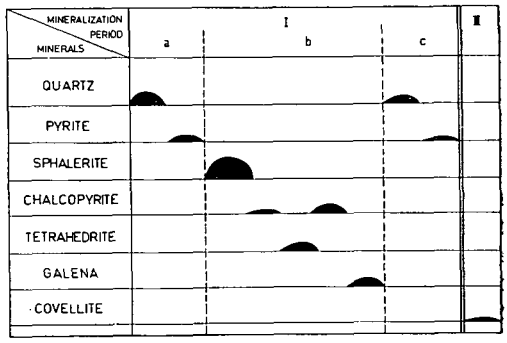
1st mineralization period contains the main ore minerals and quartz *I* which is the oldest component. The ores crystallize in the following sequence: pyrite *I* — sphalerite with partial overlapping with the younger chalcopyrite — tetrahedrite — galena. At the end of the first period a younger generation of quartz and pyrite *(II)* originated.

2nd mineralization period is monomineral and belongs to a pinkish Mn-calcite cementing the older minerals. The locality has been studied in detail by MR. AYHAN ERLER, M. S., as a part of his M. S. thesis at METU, Ankara.

Harami, Kabadüz district, Ordu vilayet (Table II)

Intensively altered country rocks are cut by ore veins with a banded structure. Some bands are composed only by the oldest fine-grained grey quartz with some

TABLE II.



Mineral sequence on the ore deposit Harami, Kabadüz district, Ordu vilayet

pyrite, some contain cavities and are filled by big grains of yellow to dark yellow—green sphalerite with some chalcopyrite *I* inclusions and by tetrahedrite, chalcopyrite *II* and galena. In druses the crystals of the named minerals occur. The youngest primary component is quartz *II* in big white individuals with small pyrite grains. Covellite is abundant in the cementation textures.

Kurnaköy, Ordu vilayet

In the ore vein filling from the mine of Ömer Şenses, a grey fine-grained quartz contains a very coarse-grained dark yellow-brown sphalerite with fine triakistetrahed-

ral crystals in cavities. Younger are the less common crystals of galena, later tabular crystals of barite, and at the last — simple rhombohedrons of calcite occur.

Association C — Pb + Zn + Cu association of hydrothermal deposits bound on the Tertiary volcanism or granitoids of the southern zone of the eastern Pontids and of western Pontids.

Muradin (Sisorta), Ordu vilayet

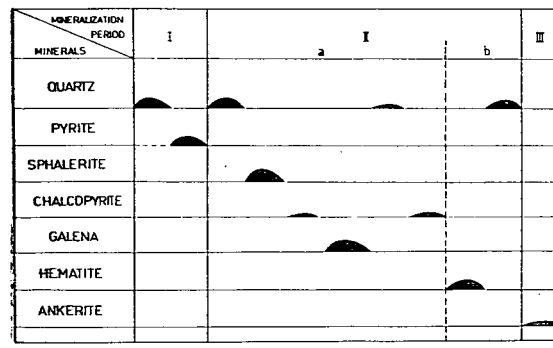
Grey-green chloritised country rock contains vein and veinlets mineralization; its predominant texture is a brecciated one, the banded texture is mostly only of short continuation.

Mineral sequence (Table III):

1st mineralization period: As the oldest components the impregnating quartz *I* with pyrite *I* occur, pyrite often being in the from of crystals in combination of cube and pentagonal-dodekahedral forms.

2nd mineralization period: After another brecciation a new portion of quartz *(II)* as white or colourless druse originated. The cavities of the druse are filled with a granular aggregate of brown to yellowish brown sphalerite, less chal-

TABLE III.



Mineral sequence on the ore deposit Muradin (Sisorta) Ordu vilayet

copyrite *I*, and common galena. The origin of minerals of this period is closed by crystallization of quartz *III* druse with fine bisphenoidal crystals of chalcopyrite *II* in the cavities. Hematite as scally specularite and the younger quartz *IV* form many bands or impregnation in the sulfide mineral aggregate.

3rd mineralization period is represented by ankerite with smaller amount of yellowish or less common white calcite.

Then originated many different secondary minerals such as cerussite, green secondary Cu minerals etc.

A detailed description of the mineral sequence from Muradin has also been submitted by ILAVSKÝ—GRENÁR [3] who found partly different sequence of some minerals and, in addition, also traces of tetrahedrite and other Cu sulfides.

Su Alti near Muradin, Ordu vilayet

For Su Alti mineralization a characteristic sign is the rhythmic structure of the younger portion of the ore vein filling. In some sections quartz-hematite bands predominate, in other sections they alternate with granular mass of galena or sphalerite.

Mineral sequence (Table *IV*):

1st mineralization period: It is composed of quartz and the main ore minerals. Quartz *I* and pyrite *I* impregnate the altered country rock in a fine aggregate or they form the central part of the brecciated sulfide mass.

TABLE IV.

MINERALIZATION / MINERALS / PERIOD	I a	I b	II	III
QUARTZ				
PYRITE				
SPHALERITE				
CHALCOPYRITE				
GALENA				
QUARTZ+HEMATITE				
HEMATITE				
ANKERITE				

Mineral sequence on the ore deposit Su Alti near Muradin, Ordu Vilayet

Then the subperiod of the main ore mineral components crystallized with brown to yellow-brown coarse-grained sphalerite with some chalcopyrite. Galena is often very coarse-grained and its aggregate is mostly fragmented.

2nd mineralization period: As the oldest seems to be the fine-grained aggregate of quartz and of scally hematite-specularite of a dark red colour. This

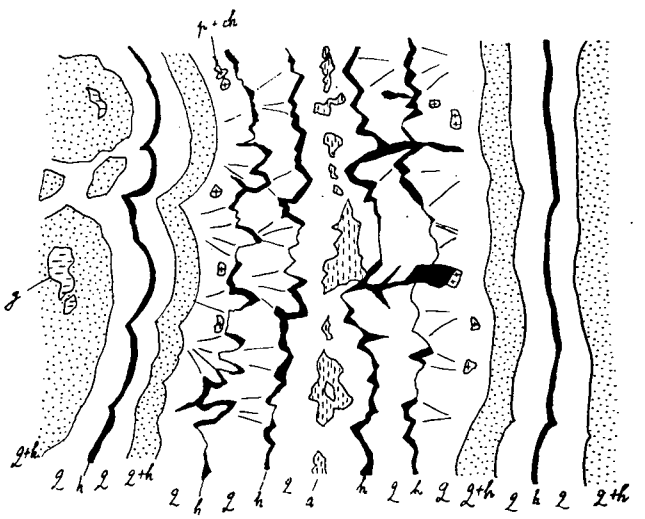


Fig. 2. A characteristic banded rhythmic structure from Su Alti near Muradin, Ordu vilayet. Quartz *(q)* and hematite *(h)* are younger then the polymetallic filling, represented here by galena *(g)* and then most of the quartz+hematite fine-grained aggregate. Pyrite and chalcopyrite are present in one quartz band, ankerite *(a)* fills the youngest geodes

aggregate is mixed with the minerals of the first period. Later, better defined banded zones of rhythmically segregated quartz and hematite originated; their thickness changes from one to another zone (between 1—10 mm mainly). The number of rhythmical banded zones varies from one place to another, the most often case is the case expressed in the enclosed table: white quartz druse — quartz + hematite — white quartz covered on crystal top by black tabules of specularite — white quartz often with crystals in cavities.

3rd mineralization period is represented by yellow-brown fine-grained ankerite cutting all the older filling and cementing its fragments.

Cakiroba, Edremit ilce, Balikesir vilayet

The main ore vein filling is formed by fine-grained white quartz *I* containing small grains of galena, yellow-brown sphalerite, and small grains of chalcopyrite and pyrite. As the youngest of named minerals seems to be galena forming small simple crystals toward the cavities. The origin of the vein filling is closed by quartz *II* in drusy aggregates, covered by small white calcite crystals.

Altinoluk, Edremit ilce, Balikesir vilayet

A fine-grained brownish quartz *I* cementing remnants of brecciated altered rocks includes the aggregate of the yellow—brown sphalerite, galena, and pyrite. Younger is the white quartz *II* as banded drusy aggregate with younger greyish calcite crystals. Another filling of these druses belongs to the product of oxidation: small crystals of cerussite, yellow pyromorphite, skeletons of smithsonite, limonite, and malachite.

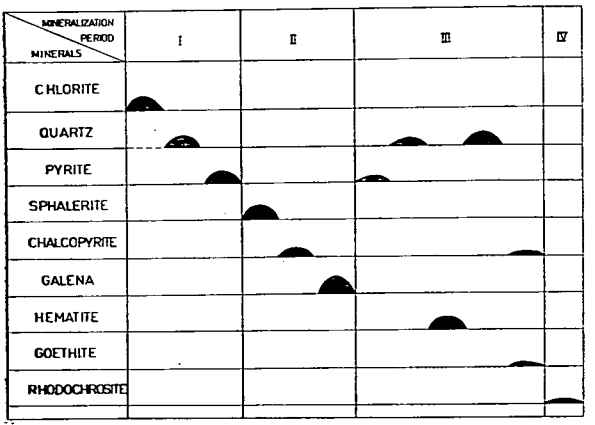
Association D — Pb + Zn + Cu association of ore veins or hydrothermal components of contact skarns in the contact zones of granitoids of Anatolids and western Pontids.

Karakoca, Simav ilce, Kütahya vilayet

Granitic rock altered by propylitization is along the dislocations mineralized by polymetallic ores with gangue in banded or brecciated structures.

Mineral sequence (Table V):

TABLE V.



Mineral sequence on the ore deposit Karakoca, Simav ilce, Kütahya vilayet

1st mineralization period: The oldest vein components are the dark-green chlorite, quartz *I*, and pyrite *I* impregnating the country rock or forming the oldest bands in the vein filling.

2nd mineralization period: It is composed mainly of ore minerals. The oldest is brown sphalerite with some inclusions of chalcopyrite which with some doubt may be parallelized with the massive chalcopyrite *I* of the ore vein filling. Galena is the youngest mineral of the period. All of them form granular or banded aggregates.

3rd mineralization period: In bands, in cavities of as breccia cementation material are the following minerals: pyrite *II* in smaller crystals or in grains together with quartz *II* and hematite as specularite scales. Characteristic younger components of the 3rd mineralization period are represented by quartz *III*, often as amethyst, with some chalcopyrite *II* in small grains or rather fine crystals of bisphenoidal type. Some groups of yellowish-brown long columnar aggregates of goethite with visible cleavage along (010) planes have been observed here too; due to its sequence position goethite may be considered a hypogene mineral.

4th mineralization period: Carbonates occur here in small amount, mainly as pink rhombohedrons of rhodochrosite sitting on the quartz *III* druse.

Association E — Pb + Zn + Cu association of ore veins or ore bodies in the areas around the intrusive massifs of Taurids.

Keban Maden, Elâzig vilayet

In the ore bodies filling on the main deposit Derebaca, a black crystalline sphalerite predominates over pyrite and galena. Pyrite *I* in form of brecciated grains cemented by sphalerite and galena has been observed as the oldest component. Younger is the second generation of pyrite with some marcasite in colloidal textures penetrating the older mass mainly sphalerite. As the youngest is to be considered the light brown ankerite and white calcite in veinlets cutting all older mineral filling.

A similar mineral sequence was mentioned by MAUCHER [1937, in GEOFFROY, 2]. KOVENKO [6] found on the main deposit Derebaca the following sequence of ore minerals: pyrite — löllingite — sphalerite *I* (Fe-rich) — chalcopyrite — sphalerite *II* (very rich in Fe 47%?) — As tetrahedrite (or rather tennantite) — jordanite — proustite — marcasite. To the last members may belong also very rare bournonite and jamesonite and newly discovered polybasite [5]. One of main ore components — galena — is lacking in the KOVENKO's sequence by obvious mistake.

In the same area in Kebandere a different scarce high-temperated polymetallic association occurs with magnetite, hematite, pyrrhotite and fluorite besides chalcopyrite, galena, sphalerite and Fe sulphides [6].

Sarikeler Ocağı near Pozanti, Adana vilayet

The brecciated filling of ore vein is formed mainly by coarse—grained black sphalerite with a greenish tint.

Mineral sequence:

1st mineralization period: Fine-grained quartz *I* with pyrite *I*.

2nd mineralization period: Crystallization of the dark-green to black sphalerite with many fine chalcopyrite inclusions took place; in its outer zone toward the cavities accumulate galena and chalcopyrite *II* as younger minerals.

3rd mineralization period: Quartz *II* together with grains of pyrite *II* forms veinlets cutting the older mass or is present as a filling of druse with imperfect crystals of sphalerite or galena.

4th mineralization period: After a distinct brecciation of the filling the pale-brown fine-grained ankerite cements the older mineral components.

The mineral sequence was not studied on deposits of association F and G of Taurids, resp. Iranids.

REFERENCES

[1] BERNARD, J. H. (*in print*): Isogenetic Pb+Zn mineral associations of Turkey. METU, Ankara.

[2] GEOFFROY, J. DE [1960]: Mine de plomb et zinc de Keban (Vil. Elâziğ). Report de MTA. No. 530, non publié, Ankara.

[3] ILAVSKY, J.—GRENÁR, A. [1960]: Contribution à la géologie et minéralogie de quelques minérais de plomb-zinc en Turquie septentrionale. Geol. práce, Zprávy **20**, 57—88, Bratislava.

[4] KIEFT, C. [1956]: Quelques remarques sur les gites métallifères du bassin du fleuve Harşit. Bull. MTA **48**, 59—67, Ankara.

[5] KINES, M. T. [1969]: The geology and the ore mineralization in the Keban area, east Turkey. Trans. Inst. Min. Metall., **78**, Aug. 1969, p. 132, London.

[6] KOVENKO, V. [1946]: Province métallogénique de plomb et de fer des Taurides (Turquie). Bull. MTA. **11**, 1/35, 53—94, Ankara.

[7] SCHNEIDERHÖHN, H. [1955]: Die Kupferlagerstätte Murgul in Schwarzmeer-Küstengebiet. Provinz Çoruh, Nordost/Türkei. Erzmetall **VIII, 10.** 468—478, Stuttgart.

[8] WIJKERSLOOTH, P. DE [1946]: Einiges über die Erzprovinz des östlichen Schwarzmeer-Küstengebietes, insbesondere über die Kupferlagerstätte von Kuvarshane (Vil. Çoruh-Türkei). Bull. MTA. **11**, 1/35, 102—120, Ankara.

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THE MINERAL COMPOSITION OF HUNGARIAN SOILS
II. SOILS OF THE BALATON REGION

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ABSTRACT

About 30 soil samples of the Balaton region (Hungary) have been investigated; all for their granulometric composition, 24 full chemical analyses were made and in 24 the mineral percentages have been determined by the diffractometer. The geographical position and the geological conditions are also sketched. — The method of determination gives also the amorphous (and poorly crystallized) content, the chemical and mineralogical composition of which has been evaluated on plausible assumptions.

In the preceeding communication of this series [1] we displayed the general points of view and purposes of our researches. Now the granulometric composition, the chemical and mineralogical composition of numerous soils from different regions of Hungary have been determined. We give in the following the results of our work on soils of the Balaton region.

I. SOILS OF BALATON-SZABADI

a) Geographical position

The cooperative "November 7" of B.-Szabadi lies along the southeastern shores of the Lake Balaton (German: Plattensee). Following the natural geography it belongs in part to Mezőföld and in part to the hilly land adherent to the Balaton. The greater part of the region lies on the comb of Enying in Mezőföld. This region is genetically and geologically much better known, than Zala County.

b) Geological conditions

The comb of Enying stretches from B.-Aliga as far as the juncture of the river Sió and the rivulet Kabóka. One has a good view of the complete section of the comb from the high banks of the Balaton near B-.Aliga where in the vertical or nearly vertical walls the upright layers show a horizontal direction. A study of these high walls — with the allowance of the eventual pinch out — reveals also the geological structure of the inner territories lying farther from the lake.

The northern part of the comb of Enying as far as the rivulet Kabóka is composed of very different layers. We find sandy and loamy layers with lignite seams alternating in thickness. The southern part of the comb, the region sinking toward the Sió is built of typical loess. One can draw the border between the two layers in the second third of the area between B.-Aliga and B.-Világos. SE of the high bank the loess sometimes reaches a substantial depth (10—15 m), since it has not been exposed to erosion as much as it was in the vicinity of the bank.

Sandy-loamy river loess and pleistocene loess, both from the Upper Pannon, are the components of the structure of the region. Under these lies the old-palaeozoic crystalline granitic slate of the Balaton region. Its today's facies has been built up as the consequence of mighthy sructural movements in the New Pleistocene.

On the top of the high bank we find also gravel tending towards SE in more or less thick layers, mainly in the higher levels, where it has shielded the sandy-loamy layers against erosion. Through erosion and deflation processes the later modification of the surface brought residues of the granitic shale to daylight.

The mineralogical examination of the bore holes set in this neighbourhood shows the prevalence of inactive minerals in the layers of the northern part of the comb of Enying; with quartz as the most common of them, felspars; calcite and dolomite are also present. Among the clay minerals illite is prevailant. In a few samples attapulgite could be detected, while others contained also montmorillonite (these two minerals have not been found in B.-Szabadi). Kaolinite was absent in all our samples. In the loess region mineralogical relations are more or less similar to the foregoing, with the important difference that there is on the whole less clay here than in the northern region.

P. STEFANOVITS [2] assings the vicinity of B.-Szabadi to the chernozem soils with chalk coating.

The third part of the area investigated by us belongs to the Sió valley, which is mostly composed of organic sediments and can be classified with the alluvial soils. The soils here are sandy—muddy alluvial formations.

c) Granulometric composition

This was determined by sedimentation of the samples formerly stripped from organic matter by hydrogen peroxide and dispersed with sodium diphosphate. It should be mentioned here that although the different dispersing materials and

TABLE I

Granulometric composition of the soils of the Balaton Region

Soil No.	Fraction μm						
	>50	20—50	10—20	5—10	2—5	<2	≦10
	I. Soil of Balaton-Szabadi						
1	24,1	29,1	9,2	6,3	12,1	19,2	37,6
2	27,0	33,0	10,0	6,0	9,0	15,0	30,0
3	23,6	33,0	7,8	5,8	8,0	21,8	35,6
4	23,9	33,6	7,7	5,2	10,0	19,6	34,8
5	22,6	36,7	6,2	5,4	7,8	21,2	34,4
6	20,7	31,8	8,2	4,0	12,3	23,0	39,3
7	18,0	39,3	6,2	4,1	11,2	21,2	36,5
8	14,0	37,0	9,0	6,0	10,0	24,0	40,0
9	33,6	30,5	4,5	1,4	7,5	22,5	31,4
10	50,1	17,5	2,6	2,6	3,5	23,7	29,8
11	40,0	18,6	5,4	4,1	8,1	23,8	36,0
12	33,9	27,5	4,8	3,1	10,6	20,1	33,8
13	33,0	22,5	7,5	7,4	8,0	21,6	37,0
14	40,0	18,9	6,3	2,8	7,4	24,6	34,8
15	30,8	30,8	5,1	3,5	9,1	20,7	33,3
16	38,6	24,1	4,0	1,9	6,3	25,1	33,3

II. Soil of Kapospula

17	5,0	44,0	11,0	5,0	9,8	25,2	40,0
18	9,0	33,6	12,2	5,3	11,3	28,6	45,2

III. Soils of Kadarkut

19	94,2	1,4	1,1	0,6	0,8	1,9	3,3
20	89,7	1,6	2,2	1,2	0,8	4,5	6,5
21	80,7	4,1	3,0	3,0	4,6	4,6	12,2
22	79,3	3,3	3,3	2,5	5,0	6,6	14,1
23	91,2	3,7	0,6	0,2	1,3	3,0	4,5
24	87,5	3,7	1,1	2,6	1,9	3,2	7,7
25	89,2	1,9	1,0	0,1	3,5	4,3	7,9
26	90,4	3,0	1,8	0,6	1,1	3,1	4,8
27	90,9	2,2	0,8	0,9	1,4	3,8	6,1
28	89,4	1,2	1,4	1,0	2,8	4,2	8,0
29	93,4	2,2	1,3	0,2	0,5	2,4	3,1
30	87,2	3,3	2,7	1,1	2,2	3,5	6,8
31	92,1	3,1	1,0	0,7	2,0	1,0	3,7
32	94,1	2,1	0,7	0,5	1,1	1,5	3,1

TABLE I (continuation)

Soil samples investigated

I. Soils of Balaton-Szabadi

1. Virgin grass (pasture) 0—20 cm
2. Virgin grass (pasture) 20—40 cm
3. A/15, wheat, fertilizer 6 q/cadastral yoke 0—20 cm
4. A/15, wheat, fertilizer 8 q/cadastral yoke 20—40 cm
5. A/15, wheat, fertilizer 8 q/cadastral yoke 0—20 cm
6. A/15, wheat, fertilizet 8 q/cadastral yoke 20—40 cm
7. A/8 wheat, fertilizer 6 q/cadastral yoke 0—20 cm
8. A/8 wheat, fertilizer 6 q/cadastral yoke 20—40 cm
9. From 5 cad. yokes, wheat 0—20 cm
10. From 5 cad. yokes, peas 0—20 cm
11. From 5 cad. yokes, barley 0—20 cm
12. From 5 cad. yokes, spring barley (fert. 7,85 q/cad. yoke) 0—20 cm
13. From 5 cad. yokes, peas (5,14 q/cad. yoke) 0—20 cm
14. From 5 cad. yokes, maize (8 q/cad. yoke) 0—20 cm
15. From 20 cad. yokes, wheat 0—20 cm
16. From 20 cad. yokes, peas 0—20 cm

II. Soil of Kapospula

17. 0—20 cm
18. 20—40 cm

III. Soils of Kadarkut

19. From C 20/1, 5 cad. yokes, potatoes 0—20 cm
20. From C 20/2, 5 cad. yokes 0—20 cm
21. From C 20/2, 5 cad .yokes 20—40 cm
22. From C 21 5 cad. yokes, maize 0—20 cm
23. From C 22 5 cad. yokes 0—20 cm
24. From C 22 5 cad, yokes 20—40 cm
25. From C 20/1, 15 cad. yokes, potatoes 0—20 cm
26. From C 21, 15 cad. yokes, maize 0—20 cm
27. From C 20/2, 19 cad. yokes 0—20 cm

28. From C 20/2, 19 cad. yokes	20—40 cm
29. From C 22, 19 cad. yokes	0—20 cm
30. From C 22, 19 cad. yokes	20—40 cm
31. Control sample	0—20 cm
32 Control sample	20—40 cm

methods do not give quite the same results, still the latter are apt for practical purposes. Sixteen soil samples have been investigated; in 4 of the both layers 0—20 cm and 20—40 cm deep, in further 12 only the layer 0—20 cm. We see the results in Table I and on *Figs. 1—6.* The grading limits are: I $<2\,\mu m$, II 2—5 µm, III 5—10 µm, IV 1—20 µm, V 20—50 µm, VI $>50\,\mu m$.

One sees different typical distribution curves, which are easily discriminated on the diagrams. Still more instructive is the comparison with the diagrams of the soils of Kapospula and Kadarkut (see below, *Fig. 7—8.*)

The granulometric composition of the sandy loam soils of B.—Szabadi shows two maxima. The first of these is always the finest fraction, the second is either the coarsest or the next coarsest part. Sandy soils, of course, have a quite different granulometric composition. The minimum lies always with the fraction III (5—10 µm), it is sometimes very flat.

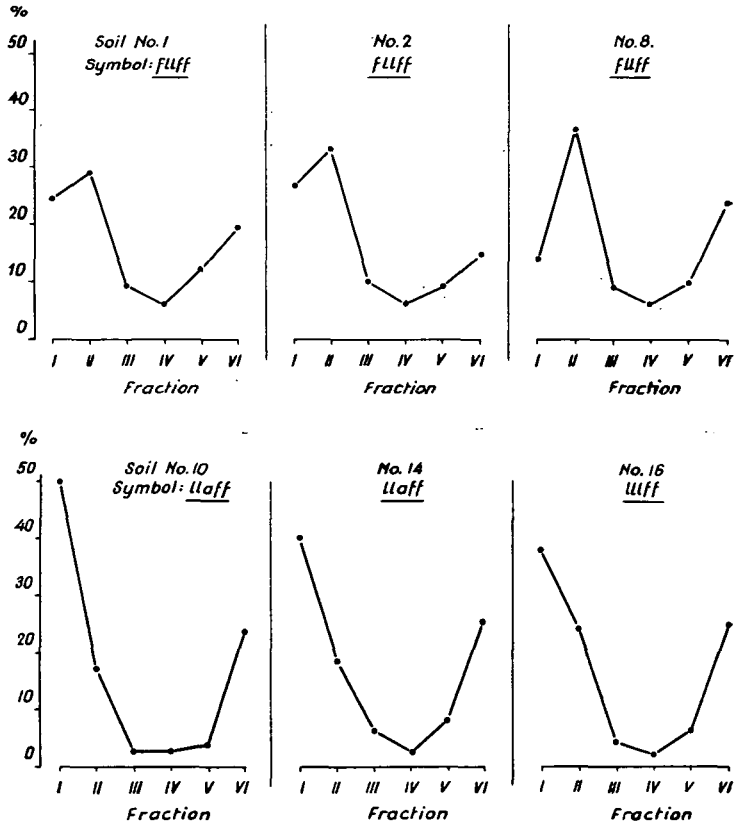

Fig. 1—6. Granulometric diagrams of the soils of B.—Szabadi

It is well known, that clay minerals are contained mainly in the finest fractions of the soil, they occur however — as will be later shown — also in the coarses fractions and in not insignificant quantities. Nevertheless the finest fractions seem to have special significance for the fertility of the soil.

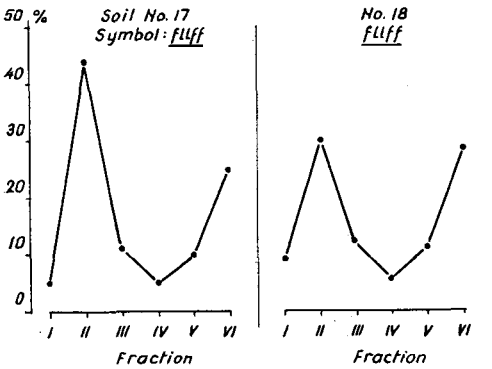

Fig. 7. Granulometric diagrams of the soil of Kapospula

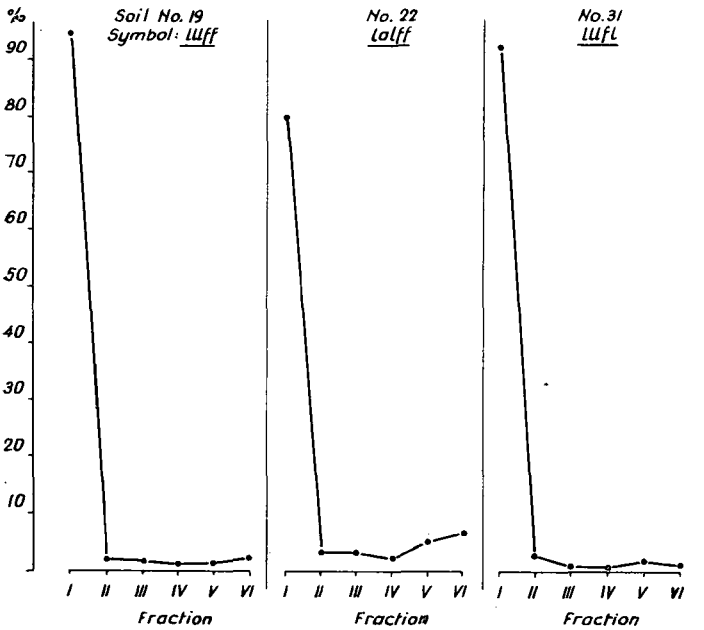

Fig. 8. Granulometric diagrams of the soils of Kadarkút

Studying the combined percentage of the fractions under 10 μm, one can see that in the soils of B.-Szabadi it amounts to 30—40,8%. There is even more in the soil of Kapospula, i. e. 40—45%, which is the most fertile among the soils inves-

TABLE II

Chemical analysis of the soils of Balaton-Szabadi and Kapospula
(Analyst: *G. Csajághy*)

Soil No.	1	2	3	4	5	6	7	8	9
SiO_2	64,20	61,82	64,70	59,73	65,08	63,37	63,96	63,34	59,36
TiO_2	0,70	0,67	0,74	0,68	0,74	0,70	0,77	0,74	0,62
Al_2O_3	10,04	9,68	10,29	9,82	9,69	9,79	10,46	10,39	9,49
Fe_2O_3	1,88	2,08	2,21	2,29	2,27	2,32	2,25	2,36	2,21
FeO	1,28	1,10	1,17	1,00	1,02	0,92	1,22	1,12	0,94
MnO	0,08	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,07
MgO	1,62	1,69	1,90	2,24	1,94	1,94	2,01	2,01	2,29
CaO	3,65	6,55	4,20	7,60	4,10	5,50	4,60	5,60	6,66
Na_2O	0,89	0,88	0,79	0,82	0,89	0,82	0,90	0,89	0,77
K_2O	1,66	1,64	1,58	1,65	1,51	1,64	1,56	1,73	1,50
H_2O-	2,71	2,29	2,22	2,23	2,21	2,17	2,15	2,25	2,47
H_2O+	2,84	3,11	3,73	2,97	3,10	3,13	3,23	3,24	3,35
P_2O_5	0,16	0,14	0,21	0,17	0,21	0,21	0,22	0,20	0,21
Carbonate CO_2	2,21	4,55	2,46	5,98	2,78	4,06	3,26	3,98	5,62
Organic matter	5,98	3,68	3,53	2,78	3,95	3,44	3,20	2,96	4,09
Whole	99,90	99,97	99,82	100,05	99,85	100,10	99,89	99,90	99,65
Fe as Fe_2O_3	3,30	3,30	3,53	3,40	3,40	3,34	3,60	3,60	3,25

Soil No.	10	11	12	13	14	15	16	17	18
SiO_2	59,99	65,73	66,66	61,67	66,78	59,49	57,99	67,92	67,71
TiO_2	0,72	0,74	0,72	0,72	0,74	0,68	0,74	0,90	0,94
Al_2O_3	9,10	11,49	11,01	10,56	11,58	9,86	9,29	13,04	13,57
Fe_2O_3	2,17	2,55	2,51	2,11	2,28	2,44	2,12	3,27	3,61
FeO	0,99	1,01	1,14	1,16	1,19	0,80	1,16	1,19	1,08
MnO	0,08	0,08	0,08	0,10	0,09	0,07	0,07	0,09	0,09
MgO	2,30	1,08	1,72	2,08	1,72	2,26	2,44	1,33	1,44
CaO	7,30	2,40	2,60	5,60	2,40	6,35	6,96	1,15	1,20
Na_2O	0,83	0,80	0,82	0,79	0,79	0,80	0,80	1,03	0,96
K_2O	1,41	1,71	1,65	1,53	1,53	1,50	1,50	1,99	1,98
H_2O-	2,06	2,90	2,52	2,44	2,72	2,54	2,46	2,38	2,52
H_2O+	4,20	3,97	3,25	3,17	3,28	3,18	3,96	2,91	3,24
P_2O_5	0,17	0,20	0,18	0,21	0,18	0,21	0,21	0,18	0,13
Carbonate CO_2	5,24	0,62	1,49	4,40	1,24	5,27	5,79	0,35	0,25
Organic matter	3,22	4,43	3,35	3,33	3,19	4,12	4,09	2,15	1,43
Whole	99,78	99,71	99,70	99,87	99,71	99,57	99,58	99,88	100,15
Fe as Fe_2O_3	3,27	3,67	3,77	3,40	3,60	3,33	3,41	4,58	4,81

tigated here. It is, on the other hand, fundamentally less in the sandy soils of Kadarkut, which give, of course, by far less good yields.

We have used the following abbreviations to mark the different granulometric types: The decreases in percentage from Fraction I to Fraction II and any further decrease is denoted *l*. The rise in percentage of a fraction is marked *f* and if it remains the same, it is denoted *a*. In this way the granulometric composition e. g. of the soil No. *14* is designated *lllff* and that of the soils No. *1* and *2* (virgin grass of B.-Szabadi) *fllff*. The formula *lllff* is very common. There occurs also *llaff*, in sandy soils, and other similar formulae. The deeper meaning of these diagrams can be understood only after further widespread determinations.

d) Chemical composition

The analyses have been performed in the Hungarian Geological Institute of Geology with the methods evolved by one of us (G. CSAJÁHGY); we can see the results in Table II together with the results for the soil of Kapospula. From these analyses one can learn naturally very important facts also concerning the mineral composition: the calcite and dolomite content, the content of P_2O_5 and apatite resp., the organic matter and trace elements. One can also draw indirect conclusions regarding the content of clay minerals, quartz and felspars. The analytical results are, however, not sufficient for the quantitative and complete determination of the mineral composition.

e) Mineralogical composition

We determined with our modified inner standard method [3] the complete mineral composition of all soils investigated. In addition to the skeleton*), carbonate and clay minerals, also the amorphous and poorly crystallized part could be determined.

We take the composition of certain soil minerals granted; this is so in quartz (100% SiO_2), calcite (100% $CaCO_3$) and dolomite (100% $CaMg[CO_3]_2$). The case is different with felspars. Owing to isomorphism, albite, plagioclases, orthoclase and microcline can be determined only with less accuracy. It is necessary to take different compositions for the different isomorphous mixed crystals and use them in appropriate cases. The accuracy of the analysis will diminish through this procedure, but it remains still very valuable for practical uses.

Table III gives the chemical composition of the most important soils minerals.

TABLE III

Chemical composition of soil minerals

	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	CO_2	H_2O+	
Quartz	100	—	—	—	—	—	—	—	
Calcite	—	—	—	—	—	56	44	—	
Dolomite	—	—	—	—	21,8	30,2	48	—	
Ca-Mont-morillonite	52	19	—	—	4	3	—	7.5	H_2O^-:15
Prochlorite	24	21	—	—	18	3	—	7	FeO:26
Klinochlor	40	22	—	—	22	—	—	16	
Muskovite	45,2	38,4	—	11,8	—	—	—	4,5	
Illite	46,5	39,5	—	6	—	—	—	7	
Kaolinite	46,5	39,6	—	—	—	—	—	—	
Albite	68,7	19,5	11,8	—	—	—	—	—	
Anorthite	43,1	36,7	—	—	—	20,1	—	—	
Orthoclase	64,7	18,4	—	—	—	—	—	—	
K-Na-Felspar 1:1	66,7	19	6	8,4	—	—	—	—	
Plagioclase 1:1	56	28	6	—	—	10	—	—	
Plagioclase 2:1	60,2	25,2	7,9	—	—	6,7	—	—	
Limonite	—	—	—	—	—	—	—	10	Fe_2O_3:90
Fluorapatite	—	—	—	—	—	54,7	P_2O_5:41,6		F:3,7

* In our notation, quartz and felspars are called skeleton minerals, although the latter are also nutrients by the virtue of their potassium content.

In the amorphous and poorly crystallized part (which contains also minerals present in small amount, like apatite, anatase etc.) we find limonite, amorphous silicic acid, amorphous aluminum oxides and hydroxides resp., the whole organic matter and also the poorly crystallized clay minerals. There are ways for the calculation of their percentages and though this calculation is by no means exact, since it accumulates the faults of chemical analysis and the diffractometric determination, it gives notwithstanding very interesting results, e. g. concerning the amount of aluminium (III)- and iron(III)-hydroxides, which make phosphoric acid insoluble. Unfortunately, the actual composition of clay minerals, namely of montmorillonite and chlorites is not accurately known.

The mineralogical composition of the soils of B.-Szabadi shows not unimportant differences. Depending on differences of the percentage of amorphous matter this variety arises from two sources, namely from the carbonate content which may be greater or lesser. Samples from the same point but of unequal depths are also somewhat divergent.

Table IV gives the results of our diffractometric determinations on 16 soil samples of B.-Szabadi. We see from the above, that quartz occurs in the amount of 34—45%, felspars 11—16%, hydromuscovite and illite together 18—27%, chlorite 5—9%, calcite 1—9%, dolomite 2—6% and the amorphous and poorly crystallized part makes 9—21%. Table 4 gives calculations of the oxide composition of the amorphous part of a number of samples. The method of calculation is expounded later under "Concluding remarks".

We also performed the calculation of the mineral composition of the amorphous part the method of which can be found also in the section mentioned; the results are compiled in Table V.

The granulometric fractions of the samples have been also analyzed with the diffractometer concerning their mineral composition; we find these results in Table VI. One may see that the mineral composition of the different granulometric fractions of the same soil sample shows characteristic differences. Here we cannot give a full discussion of facts, we allude only to our finding that also the coarser fractions (over 10 μm) contain substantial amount of clay minerals. The quartz content diminishes with the diameter of the grains, but there is still a considerable part in the fraction < 2 μm. Felspars, on the other hand, appear only exceptionally in the finest fraction.

II. SOIL OF KAPOSPULA

We obtained only two samples of this very fertile soil from the same point, but of two different depths.

a) Geographic position

Kapospula is lying on the border of two landscapes. It is customary to draw the border between the landscape of Outer Somogy and the Tolna-Baranya hilly country with the Dombóvár—Kaposvár railway line. It is, of course, not possible to exactly separate the two regions by such an artificial line, since the transition is continuous. The region of Kapospula rather belongs to Outer Somogy morphologically and geologically.

b) Geological conditions

The area of Outer Somogy is covered with loess and sand. The loess is of the same age as the younger layers of the Pleistocene loess, which covers part of Trans-

TABLE IV

Mineral composition of the soils of the Balaton region

Mineral	Balaton Region											
Soil No.	1	2	3	4	5	6	7	8	9	10	13	14
Quartz	39	44	36	34	45	36	41	35	37	40	34	40
Felspar	14	15	11	12	11	12	16	13	14	13	12	13
Muskovite+illite	19	19	27	22	22	18	18	22	23	20	24	23
Chlorite	6	5	5	5	6	5	5	6	5	6	6	7
Calcite	3	8	2	9	2	5	4	5	5	6	5	5
Dolomite	2	3	3	3	3	3	3	4	6	6	4	3
Amorphous	17	6	16	15	11	21	13	15	10	9	15	9
In the amorphous part:												
SiO_2	5	—	7	6	1	9	8	7	—	—	6	
Al_2O_3	1	—	—	1	2	3	2	1	—	—	1	
Fe_2O_3	3	3	3	3	3	3	3	3	3	3	3	
Organic matter	6	3	4	3	4	3	3	3	4	3	3	
Sum of clay minerals +organic matter	31	27	36	30	32	26	26	31	32	29	33	
Fraction ≦ 10μm	37,6	30,0	35,6	34,8	34,4	39,3	36,5	40,0	31,4	29,8	37,0	34,8

TABLE IV (continuation)

Mineral | Boden No.	Balaton-Szabadi				Kapospula		Kadarkút					
	15	16	16a	16b	17	18	20	23	24	29	30	31
Quartz	38	41	37	39	41	38	66	56	63	62	64	65
Feldspar	13	12	13	14	15	13	10	11	12	10	14	13
Muskovite + Illite	24	26	24	25	24	24	7	10	4	8	3	1
Chlorite	6	6	9	6	5	9	2	1	1	2	2	1
Calcite	5	4	2	1	—	—	—	—	—	—	—	—
Dolomite	5	4	3	2	—	—	—	—	—	—	—	—
Amorphous	9	12	12	13	15	16	15	22	20	18	17	20
In the amorphous Part:												
SiO_2	—	1	5	4	4	7	14	22	17	17	15	17
Al_2O_3	—	—	—	1	3	3	—	—	1	—	—	1
Fe_2O_3	3	3	3	4	2	4	1	—	1	—	1	1
Organic matter	4	4	4	3	4	2	—	1	1	1	1	1
Sum of clay minerals + organic matter	34	36	37	34	33	35	9	12	6	11	6	3
Fraction ≦ 10μm	33,3	33,3	—	—	40,0	45,2	6,5	4,5	7,7	3,1	6,8	3,7

danubia. According to the investigations of A. VENDL [4] the youngest loess layers of Hungary can be classified with the second glaciation of the Würm time range; this statement has been secured by newer investigations. We can find in the young loess a number of buried soil niveaus on grounds of the explorations and determinations of P. STEFANOVITS [5]; these show the climatic changes characterizing the interglacial periods. In this way we can detect these buried soil niveaus also in the area of the Outer Somogy landscape unit.

G. BIDLÓ [unpublished researches] investigated the mineral composition of three sections. The lines obtained with a simple Debye-Scherrer camera and Fe K_α radiation show quartz to be the principal component, while also calcite and felspar are present. Illite is the main clay mineral and in the upper layers also kaolinite may be detected (Nagyberek 0—10 cm). In the lower layers kaolinite disappears and in the loess of the mother rock only illite lines are present. All these three sections lie on the railway line Dombóvár-Kaposvár; in the two outer ones the upper layer contains kaolinite, in the middle one (from Báté) it is absent. All these results are qualitative.

c) Granulometric composition

This is similar in both samples of the same point (0—20 cm and 20—40 cm) and is of the type *fllff;* the percentual figures are given in *Fig. 7.* The finest fraction <2 μm amounts in the upper layer to 25,2 % and in the lower to 28,6 %; both are very substantial and the latter is the highest among the soils of the Balaton region investigated by us. The second-finest fraction (2—5 μm) is also relatively high (9,8 and 11,3 % resp.). Therefore the soil contains little amount of sand >50 μm.

e) Mineralogical composition

One can draw the conclusion already from the chemical analysis — but also from the exterior of the soil samples — that the soils of Kadarkut are typical sandy

TABLE V

Calculated mineral composition of „amorphous" part of the soils of the Balaton Region, % of the soil

Soil No.	Amorphous $SiO_2 \cdot H_2O$	Limonite FeOOH	Anatase, TiO_2	Organ. matter	Moisture, H_2O-	Sum	Dt. diffractometr.
1	5,6	2,1	0,7	6,0	2,7	17,1	17
2	—	2,3	0,7	3,7	2,3	9,0	6
3	8,3	2,4	0,7	3,5	2,2	17,1	16
4	8,4	2,5	0,7	2,8	2,2	16,6	15
5	1,2	2,5	0,7	4,0	2,2	9,4	11
6	10,6	2,5	0,7	3,4	2,2	19,4	21
7	3,8	2,5	0,8	3,2	2,2	12,5	13
8	8,3	2,6	0,7	3,0	2,2	16,8	15
9	2,0	2,4	0,6	4,1	2,5	11,6	10
10	—	2,4	0,7	3,2	2,1	8,4	9
13	7,1	2,4	0,7	3,3	2,4	15,6	15
14	5,7	2,5	0,7	3,2	2,7	14,8	9
15	0,3	2,7	0,7	4,1	2,5	10,3	9
16	—	2,4	0,7	4,1	2,5	9,7	12
17	4,9	3,6	0,9	2,1	2,4	13,9	15
18	7,1	4,0	0,9	1,4	2,5	15,9	16
20	12,8	0,4	0,3	0,9	0,4	14,8	15
23	22,4	0,2	0,4	0,8	0,3	24,1	22
29	16,9	0,9	0,4	1,0	0,5	19,7	18
31	17,3	0,4	0,2	0,7	0,4	19,0	20

TABLE VI

Mineral composition of the different granulometric fractions of the soils of the Balaton Region, weight %

Fraction μm	Quartz					Felspar					H. musk.+ Illite					Chlorite					Calcite					Dolomite					Amorphous				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
>50	67	57	47	44	59	12	22	15	22	14	4	11	5	5	3	—	—	2	1	1	1	—	2	2	1	3	—	4	4	1	13	10	25	22	21
20—50	49	50	49	43	55	23	18	14	15	13	6	13	13	14	7	3	3	3	2	2	1	1	2	2	—	3	3	4	4	3	15	12	15	20	20
10—20	40	42	42	49	42	16	15	16	14	17	17	15	26	22	18	6	9	11	8	8	1	4	2	5	2	3	2	3	4	4	17	13	—	—	9
5—10	33	36	28	30	34	15	12	21	15	19	20	33	34	28	26	12	11	13	15	11	1	6	2	10	2	2	2	2	2	3	17	—	—	—	5
2—5	28	22	28	18	29	17	13	10	13	16	32	24	42	30	26	13	10	15	15	16	1	18	5	22	3	1	2	—	2	1	8	—	—	—	9
<2	15	28	23	15	26	7	—	—	—	—	43	26	55	50	48	15	13	13	11	15	5	33	4	26	7	—	—	15	—	4	15	—	—	—	—
	6	7	8	9	10	6	7	8	9	10	6	7	8	9	0	6	7	8	9	10	6	7	8	9	10	6	7	8	9	10	6	7	8	9	10
<50	49	62	52	48	49	15	14	17	10	16	8	—	—	16	12	2	3	2	3	1	2	2	3	3	4	7	4	6	9	10	17	15	20	11	8
20—50	45	60	44	46	44	17	17	15	14	16	11	6	16	15	12	2	2	5	3	5	1	2	2	3	4	3	3	6	11	12	21	10	9	8	7
10—20	35	39	39	36	33	9	16	16	18	14	22	19	24	20	28	10	6	6	7	9	3	3	2	5	7	5	4	5	6	5	16	13	8	8	4
5—10	36	34	35	39	26	17	14	14	13	13	33	23	23	23	30	8	14	8	9	10	3	2	5	3	6	3	3	2	4	6	—	9	13	9	9
2—5	26	24	33	23	16	10	19	13	10	—	31	35	22	37	50	12	13	14	15	15	8	4	7	6	17	3	—	3	4	2	10	5	8	5	—
<2	18	17	17	10	13	10	—	—	—	—	22	51	46	62	42	7	15	13	16	11	15	8	13	8	4	7	—	—	4	3	21	9	11	—	27
	15	16	17	18		15	16	17	18		15	16	17	18		15	16	17	18		15	16	17	18		15	16	17	18		15	16	17	18	
>50	44	47	63	53		15	12	20	20		12	15	3	5		1	3	1	—		4	3	—	—		8	8	—	—		16	12	13	22	
20—50	37	41	61	51		21	15	20	22		14	14	3	5		3	3	1	2		2	3	—	—		8	15	—	—		15	9	15	20	
10—20	35	32	45	51		16	19	17	20		20	19	16	11		7	11	4	5		3	5	—	—		7	5	—	—		12	9	18	13	
5—10	31	28	—	—		12	11	—	—		28	38	—	—		9	9	—	—		2	4	—	—		5	5	—	—		13	5	—	—	
2—5	22	13	19	21		10	8	10	—		40	61	48	45		10	13	16	24		5	3	—	—		2	2	—	—		11	—	7	10	
<2	9	11	13	10		—	—	—	—		58	70	55	51		15	12	14	22		5	7	—	—		3	—	—	—		10	—	18	17	

TABLE VI (cont.)

Fraction μm	Quartz	Felspar	H. musk. + Illite	Chlorite
	20 23 24 29 30 31	20 23 24 29 30 31	20 23 24 29 30 31	20 23 24 29 30 31
> 50	64 52 69 62 69 66	16 12 14 11 13 11	— 11 — 5 — —	1 1 — 2 — —
20—50	52 54 52 42 51 52	18 17 22 27 19 23	13 8 10 13 14 6	2 2 2 3 3 2
10—20	48 52 53 43 50 48	20 19 18 24 23 17	17 18 11 17 14 12	3 4 5 6 4 3
5—10	48 50 53 42 53 55	35 10 14 21 17 15	12 19 16 19 15 10	5 5 3 8 5 2
2—5	47 52 53 40 56 58	22 13 20 17 16 21	16 16 10 20 13 11	15 4 7 10 3 3
< 2	35 29 27 17 38 29	12 14 13 — 13 —	15 40 41 28 21 20	7 7 7 15 3 15
	Calcite	Dolomite	Amorphous	
> 50	— — — — — —	— — — — — —	19 24 17 20 18 23	
20—50	— — — — — —	— — — — — —	15 19 14 15 13 17	
10—20	— — — — — —	— — — — — —	12 7 13 10 9 20	
5—10	— — — — — —	— — — — — —	— 6 14 10 10 18	
2—5	— — — — — —	— — — — — —	— 16 10 13 12 7	
< 2	— — — — — —	— — — — — —	31 — 12 40 21 36	

Since the soil of Kapospula is the most fertile among our samples, we point to the connection between the amounts of the finest fractions regarding the fertility; one can that see, naturally, in other cases too.

d) Chemical composition

These data are shown (together with the results for the soils of B.—Szabadi) in Table II. The high content of Al_2O_3, K_2O and H_2O+ is conspicuous; there is, however, only a small amount of carbonate — CO_2 present. It is, of course, impossible to determine quantitatively the amounts of the said minerals by chemical analysis. Organic matter as well as P_2O_5 is present in moderate percentage.

e) Mineral composition

This is, on the whole, very similar to that of the soils of B.—Szabadi, only the clay mineral part is higher and also the finely divided amorphous part ($<10\,\mu m$). Carbonates could not be detected with the diffractometer, although a very small amount can be present. The full data are contained in Table IV.

III. SOILS OF KADARKUT

a) Geographical position

The soils investigated lie in the sediments of the rivulet Rinya. The mother rock is pleistocene river sand, with a few pleistocene loess patches. The pleistocene sand is composed of sharp-edged grains. Also the degradation area of the rivulet is derived from sedimentary rocks, so the mineral composition is very versatile.

b) Geological conditions

Based on the above composition we draw the conlusion that the minerals mentioned consist mainly of the detrimental products of the Mecsek Mountains. The group of minerals originating from the loess completes them; the latter contain in the first line quartz, also calcite, which, however, is often dissolved and dissappears during the formation of the soil.

c) Granulometric composition

This is fairly similar in the soils of Kadarkút, at least qualitatively. In all the relevant soils the grain size of the largest fraction, i. e. 79,3—94,2 % is over 50 μm. Therefore the other fractions can amount to only a few percent; so 20—50 μm 1,4—4,1 %, 10—20 μm 0,8—3 %, 5—10 μm 0,1—3,0 %, 2—5 μm 0,5—5,0 % and $<2\,\mu m$ 1,9—6,6 %. The symbols as expounded above are *IIIff, IIfff, IIffff* etc. Oving to the very small deviations there is hardly any difference between them. Some of these distribution diagrams are shown in *Fig. 8.*

d) Chemical composition

As seen in Table VII these soils are very rich in silica (89,18—91,12 %). Alumina amounts to 4,09—5,03 %; $FeO + Fe_2O_3$ to 0,92—1,27 %; MgO to 0,14—0,32 %; CaO to 0,40—0,65%; Na_2O to 0,67—0,85%; K_2O to 0,78—0,94%; carbonate-CO_2 is absent. Organic matter makes 0,21—0,92 %, total iron as Fe_2O_3 amounts to 1,00—1,34 %; H_2O+ to 0,62—0,83 %, TiO_2 to 0,18—0,40 %; MnO to 0,03—0,07% and P_2O_5 to 0,03—0,11 %. It is clear that we have mostly quartz and felspar particles with very little clay and organic matter; the natural fertility must be very low. soils. As a matter of fact, we have found 56—66 % quartz and 10—14 % felspars in them; carbonates are missing. The total of the clay minerals is 2—11 %; organic matter is present only in small quantity, 0—1 %; see Table IV. The sum of clay minerals and organic matter makes 3—12 %, there is 15—22 % of amorphous part.

TABLE VII

Chemical Analysis of the soils of Kadarkut
(Analyst: *G. Csajághy*)

Soil No.	19	20	23	29	31	32
SiO_2	90,11	89,77	90,04	89,69	90,77	91,12
TiO_2	0,30	0,30	0,40	0,42	0,20	0,18
Al_2O_3	4,56	4,53	4,27	4,45	4,09	4,10
Fe_2O_3	0,52	0,40	0,20	0,76	0,37	0,55
FeO	0,43	0,68	0,72	0,22	0,57	0,55
MnO	0,04	0,06	0,04	0,04	0,03	0,03
MgO	0,29	0,21	0,22	0,25	0,14	0,18
CaO	0,50	0,55	0,50	0,50	0,50	0,55
Na_2O	0,69	0,74	0,68	0,72	0,72	0,67
K_2O	0,90	0,87	0,82	0,85	0,78	0,79
H_2O-	0,23	0,37	0,27	0,27	0,35	0,23
H_2O+	0,71	0,77	0,83	0,76	0,67	0,73
P_2O_5	0,05	0,07	0,11	0,06	0,05	0,04
Carbonate CO_2	0,00	0,00	0,00	0,00	0,00	0,00
Organic matter	0,75	0,89	0,83	0,71	0,72	0,21
	100,08	100,21	99,93	99,70	99,96	99,82
Total Fe as Fe_2O_3	1,00	1,15	1,00	1,00	1,00	1,05

Through a microscope it is possible to detect very small quantities of zircon magnetite, kyanite, garnets, amphibol and apatite. The fertility of these soils is in accord with this mineral composition. In spite of this, they can give still agriculturally satisfactory crops if properly cultivated.

IV. CONCLUDING REMARKS ON THE MINERAL AND AMORPHOUS COMPOSITION

Our first communication [1] alludes already to the known role of the different soil minerals. In our opinion the knowledge of the mineral composition of a soil is of vital importance in its assessment, although it is mostly very little appraised.

All soils investigated contain quartz in great proportion (34—66 % *i. e.* from one to two thirds). Felspars are always present in amounts of 10—16 % and this is often overlooked in works on soil science. But the most valuable in the soil are the clay minerals, in the first line hydromuscovite-illite and chlorites, sometimes together with montmorillonite and kaolinite; the latter two mostly in moderate amounts. It is very important, whether carbonates are present or not, since the plant needs calcium as well as magnesium. Too much carbonates is of course not desired, neither are clay minerals over 50—60 %, since in this case the rootlets of the plant cannot grow unresistedly during the dry period.

Besides the minerals treated above, there are others present in very small amounts (see above, III *e*); their role, although slighter, is still important.

The soil minerals are often poorly crystallized and there are also really amorphous parts of the soil, which are exceedingly important. Up to now no method has been employed for the determination of the amorphous content of the soil. With our modified inner standard method [3] this content can easily be determined; in our soil samples it amounts to 6—22 %. But it is also possible to make calculations concerning the composition of this amorphous and poorly crystallized part; these

conclusions are naturally somewhat less reliable than the direct determinations, since they are founded on certain assumptions.

Two kinds of calculations can be made; one can determine the oxide composition and the mineral composition of the amorphous and poorly crystallized part. In the first case, one adds the SiO_2 amounts calculated from the diffractometrically determined percentages with the aid of their known chemical composition and subtracts the SiO_2 sum obtained in this way from the result of the chemical analysis (which, of course, must be exact); the difference is contained in the amorphous part. We get so the composition of the latter and the sum of oxides calculated so must give the amount of the amorphous and poorly crystallized part determined diffractometrically (there is of course some experimental error). Organic matter belongs also to the amorphous part. We see the data so obtained in Table IV.

Concerning the mineral composition of the amorphous part we made the assumption in this work that all Fe_2O_3 is contained in it in the form of limonite, FeOOH; therefore we add an eighth of the Fe_2O_3 percentage to it from the chemically bound water, H_2O+ and we obtain so the limonite percentage (which is wholly amorphous). Now we add the SiO_2 content of the diffractometrically determined minerals and subtract the sum from the result of the chemical analysis; the difference got is amorphous, combined with the rest of the surplus water obtained in the same way from the calculated and the chemically found H_2O+ it gives silicagel, its formula being $SiO_2 \cdot xH_2O$. It is not clear if the surplus Al_2O_3 should be treated in this way or it should — at least partly — be considered as belonging to a poorly crystallized clay mineral. But the amorphous silica, the limonite, the chemically found TiO_2 which we consider to be anatase, the organic matter and the moisture, i. e. H_2O-, constitute in our analyses the amorphous part, the mean difference being about 2 % abs. One cannot expect a more exact coincidence because errors of the same sign may add. By the way we used here for the composition of the felspar albite (or plagioclase) the proportion albite: anorthite = 2:1, which is also an approximation only. The calculation process could be, of course, refined or altered.

It is well known that the knowledge of limonite and aluminium hydroxide content is very important, since these minerals make phosphoric acid and its salts insoluble.

REFERENCES

[1] KRIZA, K., NÁRAI—SZABÓ I.: Acta Geol. Akad. Sci. Hung., in press.

[2] STEFANOVITS, P.: Die Böden Ungarns. Akadémiai Kiadó, Budapest 1963 (in Hungarian).

[3] PÉTER, É.: Lecture held at the Conference for Building Materials, Warshaw 1967.

[4] VENDL, A.: Studien über den Löss der Umgebung von Budapest. Neues Jahrb. f. Min. Geol., A 69, 1935, 117.

[5] STEFANOVITS, P.: Untersuchungsangaben der begrabenen Bodenschichten im Lössprofil von Mende. Földrajzi Közl., (Geograph. Mitteilungen) 13, 1965, 339.

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GEOHISTORICAL BACKGROUND OF THE POTENTIAL HYDROCARBON RESERVES IN HUNGARY

V. DANK and I. BODZAY

INTRODUCTION

Year by year the importance of the hydrocarbons increases the world over, the countries increase their efforts to find more and more new deposits. In the appraisal of the perspectives of exploration both the geological and the economic conditions are equally decisive. The study of the amount of the prospective hydrocarbon reserves and of their probable distribution in space is a geological task, while the rentability analysis of the exploration is an economic problem.

The study of the geological conditions in the Carpathian Basin is motivated by the following considerations:

— The now-existing hydrocarbon deposits of Hungary were formed following the Alpine orogenesis. The accumulated desposits in the Early Palaeozoic period must have been mobilized and dispersed under the influence of the Variscan orogenesis, while those which were accumulated in Late Palaeozoic—Mesozoic time underwent in the same way the effect of the Alpine orogenesis.
— The Lower Palaeozoic mother rocks which were metamorphosed during Variscan orogenesis, lost their hydrocarbon contents, thus their potential reserve was not sufficient for the formation of hydrocarbon as early as Permian—Mesozoic time. Our attention has therefore been directed to the post-Variscan events.
— In Late Palaeozoic—Mesozoic time the area of the Carpathian Basin was part of the geosyncline of the Tethys, and in the Neogene it became the basin of the Pannonian inland sea. In the interest of an easier recognition of the relationships, we have therefore to consider the entire Pannonian Basin as well as the area of the Tethys surrounding it.

The purpose of the present concise review is to make known the fundamental directions with a view to such a long-term exploratory policy, according to which the exploratory operations have been made for 5 years with high economic efficiency. The paper is the first part of a long-range, collective multi-phase exploratory programme. Beside being an initiative, it is to determine the activities to be done in the future.

Even in this place we have to express our thanks to ELEMÉR SZÁDECZKY-KARDOSS, Academician, Secretary of the Earth Sciences and Mining Division and to JÓZSEF FÜLÖP, Corresponding Member of the Hungarian Academy of Sciences, who have for nearly 3 years inspired us and consulted with us in words and in writing, to GÁBOR PANTÓ, Corresponding Member, for his very precious remarks, to BARNA GÉCZY, D. Sci., for his complements showing new aspects, to KÁLMÁN BALOGH,

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FACIES BELTS AND PRE-ALPINE MORPHOLOGY OF THE TETHYS

On the basis of the data of the hydrocarbon exploration and development drillings made by the Hungarian Crude Oil and Natural Gas Trust, the basement of the Hungarian part of the Pannonian Basin is built *up of alternating belts* of Upper Palaeozoic—Mesozoic sedimentary rocks and crystalline — metamorphic formations [E. R. SCHMIDT, 1957]. In the area of our country four Upper Palaeozoic—Mesozoic belts and five crystalline—metamorphic trends separating and fringing them can be discerned [GY. WEIN, 1970]. In some of the mountains each belt is represented by outcrops. Corresponding to them, they are named the Bakony-, Bükk-, Mecsek- and Villány belts. T. SZALAI and GY. WEIN have given special names to the different crystalline—metamorphic belts.

The Upper-Palaeozoic—Mesozoic sequences of the Hungarian Central Mountains, and consequently, of the belts under consideration, *are different* [E. VADÁSZ, 1953] as manifested by both the vertical subdivisions and thicknesses of the sequences, and their lithological and palaeontological characteristics. Within certain belts the development is of the same type.

A great number of references have been published in Hungary on the *connections between* the Central Mountains and the Alpine-Carpathian-Dinaric areas. The geological connections of the Transdanubian Central Mountains with the Eastern Alps, the Gemerides and the Western Carpathians have been known since the beginning of this century. The Inner-Dinaric and South-Alpine characteristics of the Bükk-Mountains, formerly supposed to be Carpathian [F. HORUSITZKY, 1961, K. BALOGH, 1964], as well as the close relationship between the Mecsek and Villány Mts. [E. VADÁSZ, 1954; J. FÜLÖP, 1966; E. NAGY, 1969] are also proved facts. Although F. HORUSITZKY's [1968] — and formerly KOBER's [1931] — assumptions are not yet proved in detail, the present studies have led to similar results: *the E and the ENE facies belts, following the chain of the Carpathians turn first to the SE, then to the WSW.*

Of the facies belts, the *South Alpine—Bükk—Inner-Dinaric* belt shows such remarkable characteristics that it can always be readily separated from the surrounding belts. These characteristics are: marine Carboniferous and marine Permo-Triassic sediments of great thickness, Triassic and Jurassic ultrabasic—basic ophiolitic volcanism (Diabase—Chert Formation), the metamorphic nature of the Upper Palaeozoic—Mesozoic formations and the Inner-Dinaric and Inner-Carpathian flysch always associated with this belt. Because of this fact at first we deal with the areal extent of this belt.

The Upper Palaeozoic—Mesozoic Bükk development can be traced from the Karawanken through the Macelj Mts. to the Bükk Mts. by means of hydrocarbon

exploratory wells drilled in the vicinity of Lepavina, Jagnjedovac, Inke, Iharosberény, Bajcsa, Pat, Budafa, Sávoly, Táska, Buzsák, Igal, Karád, Dinnyés, Bugyi and Tóalmás. In conformity with our assumption, such type of formations has also been reached by wells drilled near Šelnica, Medjimurje, Dravsko-Središte, Varašdin, Slanje, Ludbreg, Križevci, Toplovač and Légrád.

Its northern boundary is represented by the Balaton Crystalline Range trending from the Pohorje Mts. to the Velence Mts. (via Logarevci, Verzaj, Sl. Gorica, Sobota, Bakoći, Martijanci, Filovci, Pördefölde, Eperjehegyhát, Pusztamagyaród, Gelse, Balatonhidvég, Ságvár), then by the Central Mountains Mesozoic as identified in boreholes at Tura near Gödöllő, S. JASKÓ [1946] assumed that the granites of the Velence Mts. was available underground here. Drilling wells at Recsk, Parádfürdő and Bükkszék have reached formations of Bükk facies, but in the NW part of the Recsk—Parádfürdő area, the mica-schist xenoliths within the andesite indicate already a crystalline basement [K. VARRÓK, 1959]. On account of the Ladinian sequence of Uppony and Szendrő, represented by cherts and quartzose and shaly rocks [M. MÉSZÁROS, 1961], the Rudabánya Mts. may belong to this zone, while the area of Perkupa and Jósvavölgy seems to belong to the Gemer facies. On the basis of their terrestrial Upper Carboniferous—Permian sequences the Zemplén Mts. are also associated to the former [M. MAHEL, 1968).

Its *Southern boundary* is indicated by the crystalline zone of Kaposfő—Mágocs [GY. WEIN, 1967] which can be traced with some interruptions from Zagreb to Kismarja (via Vrbovec, Cerje, Mosti, Szenta, Kutas, Jákó, Kaposfő, Cegléd, Túrkeve, Püspökladány, Furta, Körösszegapáti, Kismarja) [GY. WEIN, 1967] and by the Törtel—Nyírlugos flyschoid zone in its foreground patterned by Jurassic limestone reefs (Hajdúszoboszló, Ebes). In Rumania the bituminous and cherty Triassic limestones, the ophiolites connected with radiolarites and the flysch formations containig Jurassic reefs in the Turda—Lipova zone of the Transsylvanian Metalliferous Mountains [P. Rozlozsnik, 1937; L. NAGY, 1958; M. ILIE, 1961; CHEORGHIU, 1961] doubtlessly belong to the Bükk facies. The connection with them can be traced by following the occurrences of the Inner-Carpathian flysch — as believed by T. SZALAI as well — through the eruptive masses of the Oraşului—Gutăiului, the Sălaj, Baia-Mare and Oas subbasins, and then the Rodnei Alps up to the Transsylvanian Basin [L. NAGY, 1958]. The Turda—Lipova zone is separated by the Gilău-Zărand crystalline zone from the different Upper Palaeozoic—Mesozoic formations of the Apuseni Mts., while towards South it is bounded by the crystalline mass of the Rusca Alps. According to K. TELEGDI ROTH [1929], the Transsylvanian Metalliferous Mts., "*following the bend* of the arch of the Balkan-Mts., fit in the continuations of the North-Serbian tuffite formations, interrupted with the Pannonian subsidence". This connection does exist there without doubt, as affirmed by drilling in Jugoslavia, at Meda, Begejci, Melnici, Bečej, Gospodinci, Temerin, Stepanovo, Silbas, Plavna, Vulkovar, Konak, Boka, Zitiste, Lazarevo, Zrenjanin, Elemir, Orlovat, Samos, Padina, Alibunar, Gloganj, Ovca, Omolica, Semberija, Korace, where flysch formations containing Jurassic Limestone reefs and serpentines have been found and by the ophiolite of the Fruska—Gora traceable as grading into the serpentine—flysch zone of Bosnia. In Jugoslavia, on the northern margin of the flysch zone the holes drilled near Mokrin, Boka, Kikinda, Crnja, Idos, Milosevo, Ada, Feketič, Rada, Turja, Sirig, Srborban, Kula, Darda, Osijek, Bizovac, Klokocevci, Nasice, Djakovo, Bosna Gradiska, Visoko Greda, and Bunjani, — and the intrusive and metamorphic

formations of the Papuk Mts. represent the continuations of the Kaposfő—Mágocs—Gyalu—Zaránd crystalline zone.

On the basis of the foregoings the *Upper Palaeozoic—Mesozoic zone,* characterized by *Bükk facies types* and covered by Cretaceous—Paleogene flysch in most of the area *can be traced from the Karawanken through the Bükk Mts. and the Transsylvanian Metalliferous Mts. to the Inner-Dinarides.* It is also without doubt according to the studies of. D. NIKOLIČ—R. KEMENCI [1970].

The Upper Palaeozoic—Mesozoic belt of the *Mecsek Mts. range* stretches from the vicinity of Sedlarča Ferdinandovac—Vizvár (through the boreholes drilled in the neighbourhood of Kurd, Tolnanémedi, Kiskőrös, Izsák, and Kerekegyháza in the Danube—Tisza Interfluve) to Nagykőrös—Szank. In the north it is bounded by the hypothetical Kaposfő—Cegléd zone, while in the south by the Mórágy—Pálmonostora (Babócsa, Pécs, Mórágy, Miske, Szank, Pálmonostora, Pusztaföldvár), crystalline zone. In the Trans-Tisza Region (E of the Tisza river), the Tertiary formations between Szentes and Gyula have not been yet penetrated by drillings so that their extension towards teh Apuseni Mts. can be only supposed. According to our hypothesis, the boreholes drilled near N. Kulzovac, Nadoljan, Velebit, Szenta, Gornibreg, Bajsa, Benicanci, Gojlo, and the Upper Palaeozoic—Mesozoic formations of Papuk Mts. mark the extension of this belt beyond the Codru Mts.

South of the crystalline zone of Mórágy, the Upper Palaeozoic—Mesozoic section of the *Villány Mts.* extends through the drilled holes of Komlósd, Kálmáncsa, Szulok, Szigetvár, Bogádmindszent and Téseny to the Villány Mts., in the southern part of the Danube-Tisza Interfluve (Érsekcsanád, Rém, Jánoshalma) to Eresztő, Pusztamérges and Ásotthalom, and farther away presumably well into the Trans-Tisza Region, up to Tótkomlós—Pusztaszöllős. This belt is separated from the Bihor zone by the Battonya—Szeged—Palics crystalline zone, regarded as the continuation of the Mórágy crystalline belt.

The Transdanubian Central Mountains, to the north of the Lake Balaton crystalline zone extend northwards into the so-called Drava zone and into the Gailtal Alps [E. VADÁSZ, 1954], while in NE direction they can be traced in the South-Gemer part [F. HORUSITZKY, 1961] of the southern zone of the Western Inner-Carpathian [M. MAHEL, 1968]. To the north of this Upper Palaeozoic—Mesozoic belt, the *middle crystalline belt* of the Eastern Alps can be traced from Kőszeg, through Mihályi and Kolarovo, to the Spiš—Gemer Metalliferous Mts. North of the middle crystalline belt there is the Upper Palaeozoic—Mesozoic belt of the *Northern Calcareous Alps,* having a completely similar development to that of the belt of the Central Mountains, which as shown by recent studies, have their continuation in the Northern Gemer and "Choč" sequences [M. MAHEL, 1961] of the northern Inner-Carpathians [M. MAHEL, 1968] East of the Zemplén Mts. these two mesozoic belts plunge underground and are re-exposed first in the *East-Alpine or Austro-Alpine* [M. MAHEL, 1968] uniformly crystalline Mesozoic belt of the Eastern-, and then of the Southern Carpathians [L. NAGY, 1958]. The outermost Mesozoic zone of the area being considered represented by the Križna, Manin and "Mantle" sequences [M. MAHEL, 1961] showing a so-called Carpathian [K. TELEGDI ROTH, 1929] or a *Central-Carpathian* [M. MAHEL, 1958] development and belonging to the central and northern (Klippen Belt) zone in the Western Inner-Carpathians. This Mesozoic development, including the Paleogene flysch, is bounded by the Outer or Flysch Carpathians extending equally in E, W and N directions. And it may be assumed that the Carpathian facies extends to the E and W into the flysch basement.

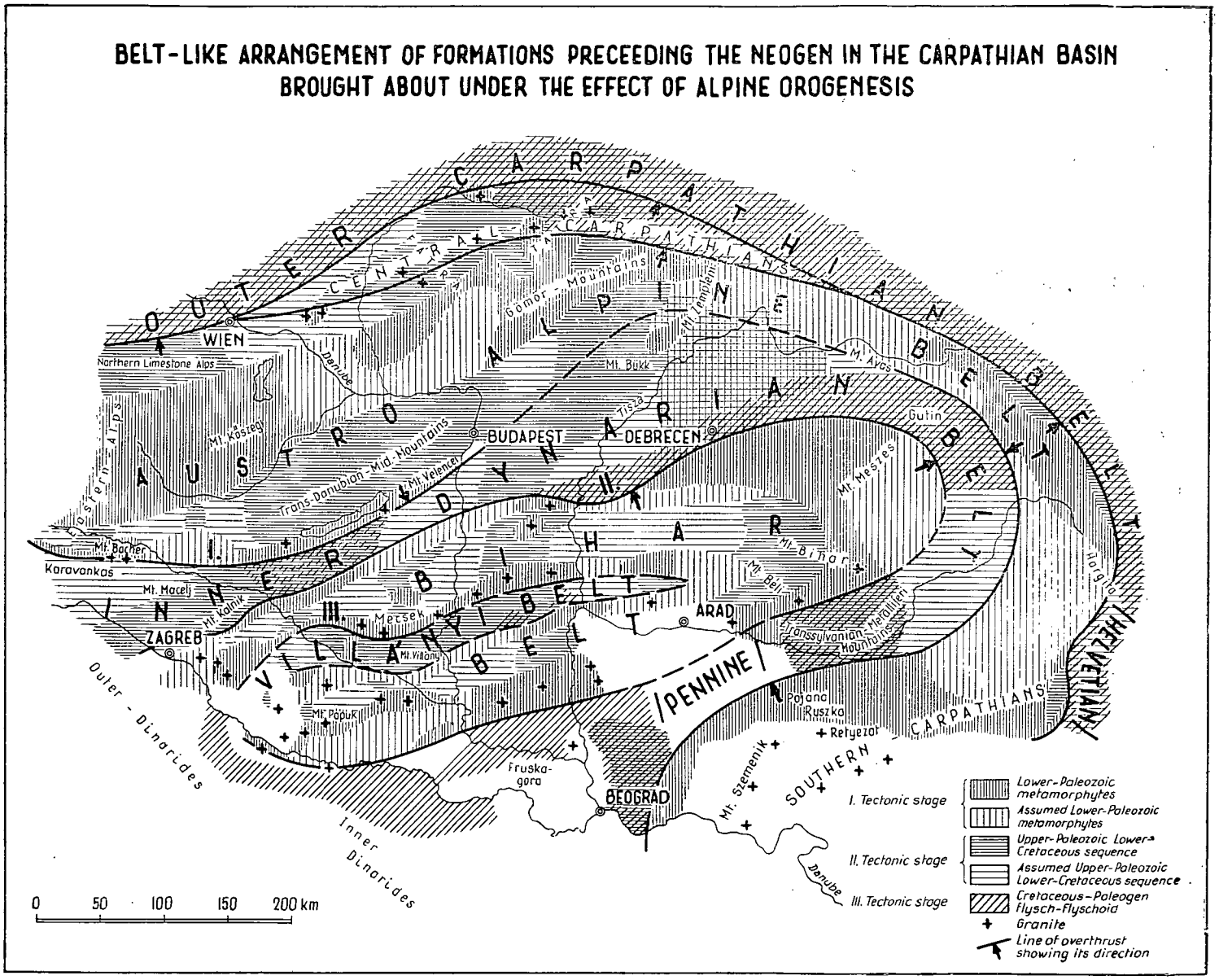
BELT-LIKE ARRANGEMENT OF FORMATIONS PRECEEDING THE NEOGEN IN THE CARPATHIAN BASIN
BROUGHT ABOUT UNDER THE EFFECT OF ALPINE OROGENESIS
OUTER CARPATHIANS
CENTRAL CARPATHIANS
INNER CARPATHIANS
ALPINE BELT
PANNONIAN BELT
MARGINAL BELT
INNER DINARIDES
OUTER DINARIDES
PENNINE
SOUTHERN CARPATHIANS
WIEN
BUDAPEST
DEBRECEN
ARAD
ZAGREB
BEOGRAD
Northern Limestone Alps
Eastern Alps
Danube
Tisza
Mt. Bükk
Mt. Ayas
Gutin
Mt. Mecsek
Mt. Villány
Mt. Papuk
Fruska-gora
Mt. Bacher
Karavankas
Mt. Macelj
Mt. Kőszeg
Mt. Velence
Trans-Danubian-Mid.-Mountains
Mt. Bihar
Mt. Bel
Transsylvanian-Medium Mountains
Pojana Ruszka
Retyezat
Mt. Szemenik
Hungarian Plain
0 50 100 150 200 km
I. Tectonic stage
II. Tectonic stage
III. Tectonic stage
Lower-Paleozoic metamorphytes
Assumed Lower-Paleozoic metamorphytes
Upper-Paleozoic Lower-Cretaceous sequence
Assumed Upper-Paleozoic Lower-Cretaceous sequence
Cretaceous-Paleogen flysch-flyschoid
Granite
Line of overthrust showing its direction

Fig. 1.

In *summary* it can be stated that *five facies belts of the Upper-Palaeozoic—Mesozoic formations in the Carpathian Basin* are known: the *Central- and Outer Carpathian* belt; the East-Alpine—South-Alpine or *Austro-Alpine* belt, which in the Zemplén Mountains is divided into two branches (Northern Calcareous Alps — Northern Gemerides, Gailtal Alps — Southern Gemeriden); the *Karawanken—Bükk —Transsylvanian Metalliferous Mts.—Inner-Dinarides* belt; the *Mecsek—Bihor—Papuk* belt, and the *Villány* belt.

In Upper Palaeozoic time the *Central- and Outer-Carpathian*—hereafter referred to briefly as *Outer-Carpathian*—belt still was a part of the North-European continent. The Lower—Triassic is characterized by the great quantity of quartzite, the Middle Triassic by limestones and dolomites poor in fossiles, the Carnien—Norian by the Keuper facies, the Rhaetian by the a pelitic—lumachelle facies. These characteristics are similar to the epicontinental, so-called "Germanic", Triassic. Therefore this belt is developed in the northern part of the Western Alps. While on the northern fringe of the Eastern Alps it can be considered a constituent of the flysch belt basement and a *continuation of the Helvetian facies* showing similar characteristics, *while the Central-Carpathian belt can be considered a tectonic window of the Helvetian facies.* The lower and middle parts of the Jurassic, having a small thickness, consist of shallow-water, cherty sandstones, shales and crinoidal limestones. A typical facies of the lower part of the Malm is the red radiolarite, while that of the Titonian is the shallow-water, cherty limestone with a pelite content increasing upwards. The Lower Cretaceous is of flysch facies.

The *Austro-Alpine facies belt* is characterized by a terrestrial Upper Palaeozoic (in the neighbourhood of Dobšina and in the Zemplén-Mts. littoral detrital—lagoonal Upper Carboniferous); by Permian quartzous porphyry, by a littoral, detrital—lagoonal Lower Triassic grading into a neritic, offshore calcareous—dolomitic Middle and Upper Triassic of great thickness with insignificant "pietra verde" traces of volcanism in the Middle-Triassic, and with a Kössen and Lunz facies in the uppermost Triassic; by a deep-water Jurassic of low thickness, lacking terrigenous materials, discontinuous and incomplete ammonitic, including sublittoral (Gresten) facies in the Lias, and shallow-water (Hierlatz) facies in the Lias and Dogger, and by a bathyal and shallow-water Lower Cretaceous.

The Upper-Paleozoic of the *Karawanken—Bükk—Inner-Dinaric* (referred to hereafter briefly just as Inner-Dinaric) belt is a thick neritic sequence of sediments interrupted by terrestrial levels. In the Alps the Lower and Upper Carboniferous separated by a hiatus, as well as the Lower Permian are near-shore detrital—calcareous sediments of grauwacke type, the Middle Permian is terrestrial (Gröden sandstone), and the Upper-Permian is a neritic Bellerophon limestone and dolomite interbedded with sandstone and gypsum. Although there are no references to the presence of Jurassic formations in the Bükk-Mts. the Triassic and Jurassic are characterized there by a pelagic sedimentation, calcareous and pelitic, and by basic and ultrabasic rocks (ophiolites) mixed with cherty schist with Radiolaria (diabase—chert formation, K. PETKOVIC, 1961). In this sense the basic volcanites of Szarvaskő, Tóalmás and Inke could have formed in the Triassic or Jurassic periods. The Lower Cretaceous is of a flysch facies. Metamorphism of various degree is significant, being characteristic of the whole Carboniferous—Jurassic sequence. These peculiarities, compared to the characteristics of the Pennine facies of the Western Alps (very thick Carboniferous, with deep-sea Triassic—Jurassic radiolarites and ophiolites, anchi-metamorphic character), make it plausible to assume that the *Inner-Dinaric*

Upper Palaeozoic—Mesozoic belt is a continuation of the Pennine facies belt of the Western Alps.

The Mecsek—Bihar belt is characterized by a thick, terrestrial Upper Carboniferous—Permian, with Permian quartzporphyry, by a transgressive (lagoonal-detrital) Lower-Triassic, a shallow-water calcareous—dolomitic Middle Triassic and Upper-Triassic becoming gradually continental from the Karnian on. The Lias having a great thickness is of the Gresten facies (Mecsek, Kiskőrös, Szank, Bihor), then towards the Jurassic it becomes pelagic, in the Malm with a net chemical sedimentation. The Lower Cretaceous is entirely represented by a regressive sequence with a break in sedimentation, and with a vigorous basic subaquatic volcanism in the Mecsek.

The poorly known *Villány belt* is characterized by a continental Upper Carboniferous and Permian, by an incomplete Triassic and Jurassic, by the Lias of Adneth facies (Eresztő, Pusztamérges, Pusztaszöllős, Tótkomlós), by a shallow-water Dogger and Malm limestones, by a Neocomian hiatus with traces of a trachydolerite volcanism and by limestones of Urgonian facies [J. FÜLÖP, 1966].

Beyond Zagreb the Bihor—Villány belt collides with the Outer-Dinarides of opposite strike. Their relation with the Outer-Dinarides is to be studied in the future. *We think it possible that the belt of the Bihor and Villány is a continuation of the Outer-Dinaric belt in the Carpathian Basin.*

According to E. VADÁSZ [1954], T. SZALAI [1958, 1959], GY. WEIN [1966, 1970] and F. HORUSITZKY [1968], the Hungarian Central Mountains and the series of strata in the belts previously distinguished are not the heteropic facies of one and the same uniform geosyncline, but they are sediments of subgeosynclines separated by isthmuses, rows of isles and seamounts. K. BALOGH [1964] does not think it necessary to justify the existing facies alterations by supposing a separating ridge; that is, in his opinion the Bükk and Gemer sediments would have settled in different parts of one and the same uniform sedimentary basin. In 1960 E. VADÁSZ has also taken a stand on that. ("There is no obstacle in the way of believing that the Triassic members of the Hungarian Central Mountains could be considered a Triassic sea starting from the Alps through the Bükk-Mts., together with the area of the Slovakian Karst with a continuous, — but dissected bottom or — possibly a geosyncline-.")*According to the idea of* KOBER, STAUB *and others, the Mesozoic geosyncline of the Tethys was a sea-basin similar to the present world oceans, with well distinguished and diversified facies and true oceanic depths* [in K. TELEGDI ROTH, 1929]. Taking into account that the Nort—German—Polish (Germanic) Triassic is continental—epipelagic, the Outer-Carpathian (Helvetian) facies is of a transitional type, the Austro-Alpine is shallow-marine — with an increasing pelite content towards the Helvetian belt [M. MAHEL, 1961] — the Inner-Dinaric (Pennine) facies is of abyssal development and of a thickness corresponding to this; furthermore that the formations of the Austro—Alpine and of the Inner-Dinaric belts from the Middle Triassic to the Lower Cretaceous do not contain any littoral detrital sediment, which would suggest the proximity of a continent ("coastless" belts as referred to by E. VADÁSZ, 1954, E. R. SCHMIDT, 1957), *the conception of* KOBER, STAUB, K. BALOGH and E. VADÁSZ [1960] *seems to be justified.* The axis of the geosyncline was formed by the Pennine belt, and its northern edge by the Germanic area. The Bihor—Villány and Outer-Dinaric belts could have belonged already to the southern half of the geosyncline. According to the statement of E. VADÁSZ [1960], "the differences in the development of our

mountains are ultimately due to a specific crust structure, as well as they are influencing factors of the later crustal movements".

The *pre-Alpine morphology* of the studied part of the Tethys can briefly be summarized as follows:

The innermost belt of the geosyncline (Inner-Dinaric belt) was covered by a shallow sea already in the *Late Palaeozoic periods* ("The geosyncline state is oldest here", F. HORUSITZKY, 1961). The surrounding parts of the area are at the same time emergent land surfaces with continental—littoral sediment form the Upper Carboniferous and with a final volcanism in the Lower Permian.

In the *Triassic,* with the progress of transgression, the sea of the Inner-Dinaric belt reached an abyssal depth and was the scenery of the initial ophiolitic volcanism of the Alpine orogenesis, which "is characteristic of the early subsidence-and-sedimentation stage in the evolution of the orogenic belts... of the marginal, partly abyssal graben-trough zone of the oceans" [E. SZÁDECZKY KARDOSS, 1968]. The neritic sedimentation at the same time shifted unto the area of the surrounding belts. In the Austro-Alpine belt a detrital—lagoonal littoral, then from the Middle Triassic a neritic carbonate sedimentation took place. Taking the statement of G. PANTÓ [1961] into account, the thin volcanic tuff layers, the so-called "pietra verde" of the Ladinian stage ("Its halmyrolytically decomposed material was transported by sea currents from remote submarine volcanic activities") may be derived from the submarine volcanoes of the Inner-Dinaric belt. The edge of the basin in the north is represented by the North-European continent, on the margin of which an epicontinental, tripartite, so-called "Germanic" Triassic has evolved. The Triassic of the Outer-Carpathian belt is a transition between the Germanic and Austro-Alpine developments. South of the Inner-Dinaric belt, in various parts of the Mecsek—Villány belt both neritic and transitional features can be found.

In the *Upper Triassic* a general regression is recognizable over the whole studied area of the Tethys. This becomes apparent in the area of the Germanic and Outer-Carpathian belt, so that the sedimentation becomes continental sublittoral (Keuper), in the Villány belt it is clearly manifested by the lack of sediments, being recognizable (Kössen and Lunz facies) even in the neritic regions (Austro-Alpine and Bihor belts).

At the end of the Triassic, at the onset of the *Jurassic period* a new transgression of the sea began which was characterized by the Gresten facies accompanied by coal formation in many places on the edges of the emerged land areas. The increasing transgression was marked by the fact that the Austro-Alpine belt became pelagic, the German and Villány areas neritic, and by the superposition of the Dogger—Malm deposits upon an older basement in several places. Simultaneously, the axis of the West-Carpathian sedimentary basin migrated to the north [M. MAHEL, 1961, 1968]. The extent of the Tethys reached its culmination at the beginning of the Malm. In the Tithonian already some symptoms of regression can be recognized, and in *Early Cretaceous* time chemical sedimentation was accompanied by the introduction of terrigenous material even in the innermost belts.

STRUCTURAL CONDITIONS OF THE PRE-NEOGENE FORMATIONS, AND CRETACEOUS-PALEOGENE MORPHOLOGY

In the area of our country "the orogenesis seems to have resulted in piling up and compression of formations that used to be distributed over larger areas" [K. TELEGDI ROTH, 1929]. In the Bakony "the marine facies of a great part of the Mesozoic sediments can only be imagined by supposing an intense piling up, because of the proximity of the Velence-Balaton crystalline belt which was terrestrial at that time..." [E. VADÁSZ, 1954]. This "...is generally recognizable in the structure of the mountains in different measure" [E. VADÁSZ, 1960]. The presence of such a compression-imbrication structure — with overthrusts similar to the classic "Litér fault" [F. PÁVAI VAJNA, 1930], — is clearly evidenced by the recent results obtained, also on the basis of deep drilling, for the Central-Mountains — e. g. the Apuseni Mountains in Transsylvania.

Similarly to the Hungarian Central Mountains, a system of compressional-longitudinal and disjunctive—transversal fractures is typical also of the belts distinguished in the present paper [E. R. SCHMIDT, 1957]. The direction of the longitudinal fractures,

SCHEMATIC STRUCTURAL SECTION OF THE OVERTHRUSTED GREAT STRUCTURAL UNITS

(Prepared by using the figure of E.R.Schmidt)

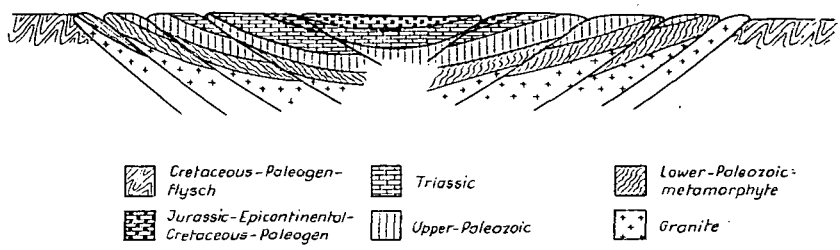

Fig. 2.

following the strike of the belts, is SW-NE and WSE-ENE, respectively, but in the Padurea Craiului-Bihor-Gilău-Codrului zone, parallel to the strike of the Eastern Carpathians, it is N-S [P. ROZLOZSNIK, 1937, M. ILIE, 1961]. In the Moma and Transsylvanian Metalliferous Mountains, just like in the Southern Carpathians, these fractures trend ENE-WSE [P. ROZLOZSNIK, 1937, M. ILIE, 1961], in the Inner-Dinarides NNW-SSE [STEVANOVIČ, 1964].

In respect of the details of the imbricated structure, *the Central Mountains and the belts under consideration are "asymmetrically two-flanked mountain structures, with an outward...* tending *movement,* and with more vigorously dislocated mountain-flanks on the side exposed to the more efficient power. The *two flanks are generally separated by a trough* having the character of a syncline" [E. R. SCHMIDT, 1954]. "It is always the southern to southeastern flanks that are more vigorously affected by tectonic deformation" [E. R. SCHMIDT, 1961]. This structural arrangement could be

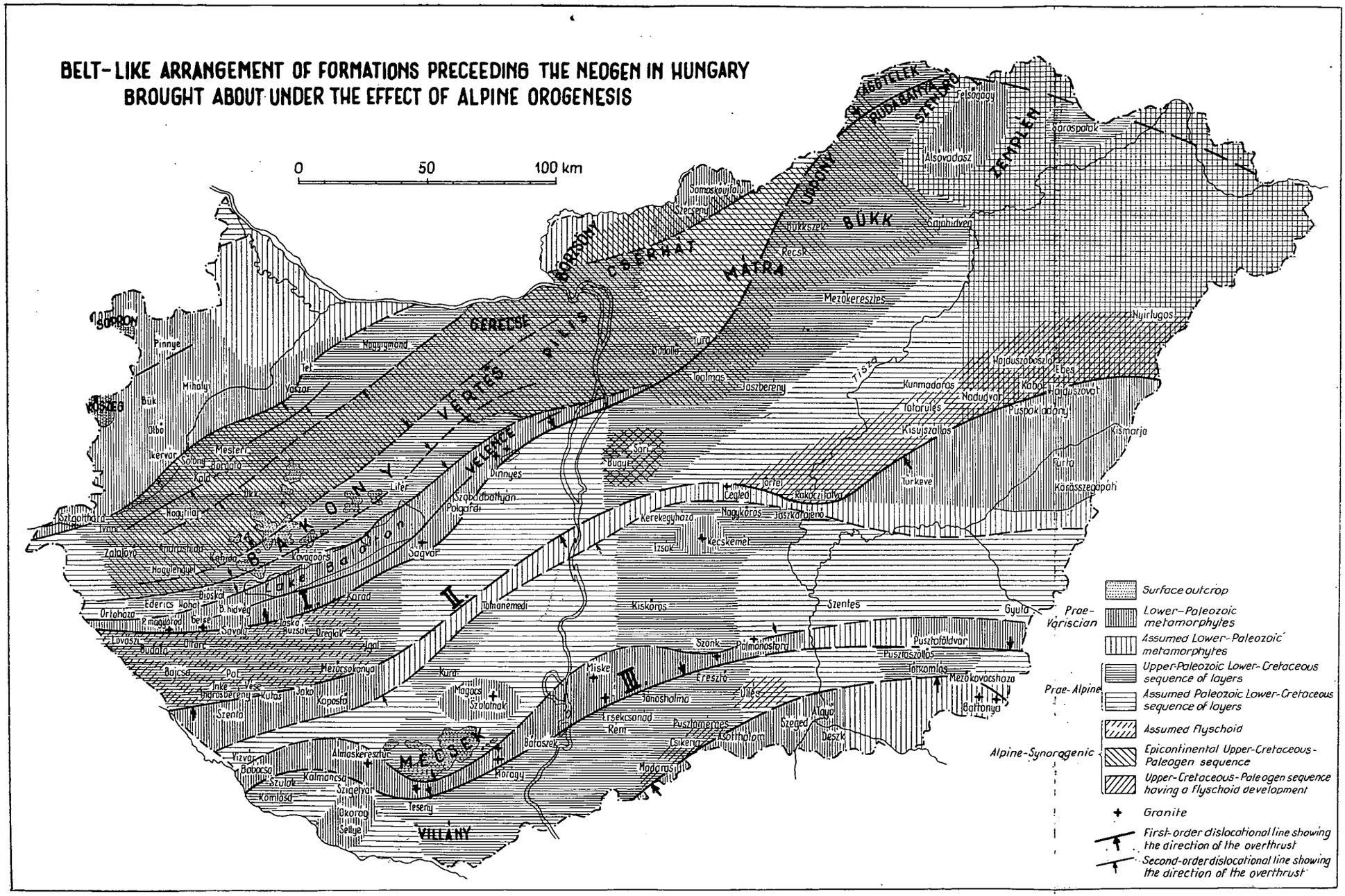
BELT-LIKE ARRANGEMENT OF FORMATIONS PRECEEDING THE NEOGEN IN HUNGARY BROUGHT ABOUT UNDER THE EFFECT OF ALPINE OROGENESIS
0
50
100 km
SOPRON
KŐSZEG
GERECSE
BÜKK
MÁTRA
CSERHÁT
VILLÁNY
MECSEK
Surface outcrop
Prae-Variscian
Lower-Paleozoic metamorphytes
Assumed Lower-Paleozoic metamorphytes
Upper-Paleozoic Lower-Cretaceous sequence of layers
Prae-Alpine
Assumed Paleozoic Lower-Cretaceous sequence of layers
Assumed flyschoid
Epicontinental Upper-Cretaceous-Paleogen sequence
Alpine-Synorogenic
Upper-Cretaceous-Paleogen sequence having a flyschoid development
Granite
First-order dislocational line showing the direction of the overthrust
Second-order dislocational line showing the direction of the overthrust

Fig. 3.

doubtlessly demonstrated in the Mecsek [E. R. SCHMIDT, 1957, G. HÁMOR, 1964], the Bükk [E. R. SCHMIDT, 1967, K. BALOGH, 1964], the northern and southern Gemerides [M. MAHEL, 1961], and most recently in the Villány Mountains [GY. WEIN, 1967]. The Transdanubian Central Mountains are, according to the concept of L. KŐRÖSSY [1963], a regional monocline with a NW dip. The prevailing dip direction in the Bakony is NW, but already H. TEGER and K. TELEGDI ROTH showed the presence of a SE dipping counter-flank in the NW Bakony Mts. (Pápa) [E. VADÁSZ, 1953]. In the course of our present studies, in the continuations under the Bakony basin-sediments we came — coinciding with the studies made by F. HORUSITZKY [1961] in the Buda-Mountains and by GY. NAGY [1964] in the Gerecse Mountains — to the recognition that the Upper Permian-Lower Carnian beds crop out from the Upper-Carnian, Norian Hauptdolomit only on the NW and SE edge of the mountains along the Balaton and Kőszeg-Mihályi crystalline zones (Borgáta, Mesteri, Tét, Káld, Dióskál, Ortaháza, Kővágóörs) on the erosional surface of the Triassic sequence, while the Hauptdolomite is covered by Rhaetian formations — with Jurassic and remainders — in the central part of the area, around its longitudinal axis (from Nagylengyel to the Gerecse). This setting applying to the entire megatectonical unit, testifies to the occurrence of a trough-like structural from having a NE—SW axis, which was named synclinorium by K. TELEGDI ROTH, syneclisis by E. VADÁSZ, and tectonic trough (geoalveous) by E. R. SCHMIDT.

From the trough-like structure of our Upper Palaeozoic—Mesozoic belts, divided into bilaterally symmetrical thrust-sheet ranges, and from the relatively small difference in altitude it is clear that progressing from the axial lines of the belts towards their edges, older and older formations follow each other, in general. *The magmatic—metamorphic zones bordering the Permian—Lower Triassic thrust-sheets are the outermost thrust-sheet ranges of the belts under consideration, in which the deepest structural stages of the Hungarian mountains are exposed.* This is also evidenced by the size of the crystalline zone alongside the Balaton (250 km long, and 5—10 km wide), moreover, by the strong tectonical influences affecting the granite [A. KŐHÁTI, 1964], further by tectonized breccia zones observable in many places (Szilágyi-1, Pécs-7) between the granite—metamorphites and the Permian—Mesozoic formations in the Mecsek-Mts. [G. HÁMOR, 1964]. *The two-phase* intrusion of the granite (basic granite—microgranite) *is just an illusion due to the present tectonical setting*, since three horizons (Lower Palaeozoic metamorphites, Lower Palaeozoic metamorphites pierced by granite dykes, and granite) of a deeper structural stage have come into a juxtaposition along reverse fault lines. In our opinion, such a mechanism may account for the tectonic contact between the so-called basic granite and the Silurian—Devonian schist sequence, lacking any contact-metamorphism, melting-in or injections an accompanied in some places (Meleg-Mountain—Antónia-Mountain) by the formation a brecciated zone reaching even 100 m in thickness [E. VADÁSZ, 1960].

Each Upper Palaeozoic—Mesozoic belt and the corresponding magmatic—metamorphic zones are, therefore, different structural stages of the same megatectonic unit. The megatectonic units are separated from one another by dislocation lines of the first order, „belts having an orogenic character", along which the edges of the structural units have been piled upon one another [L. KŐRÖSSY, 1963].

I. The *„Balaton line"* [T. SZALAY, 1958], which is named by E. VADÁSZ [1954], together with the second-order dislocation lines, „the belt of the South Alpine piling", is the overthrust zone separating the Inner-Dinaric and Austro-Alpine mega-

tectonic units on the southern boundary of the Balaton crystalline zone [L. DUBAY, 1962, L. KŐRÖSSY, 1963] and may be considered a continuation of the fault in Gailtal, Austria. In our country it is accompanied by the Upper Eocene andesite volcanoes (Hahót—Ederics, Velence Mts., Recsk), but a significant Tertiary volcanism is associated with it in Serbia, as well. Along this dislocation belt the *Inner-Dinaric unit thrusted under the Austro-Alpine* one. In the territory of our country it is proved by the following: in the South Zala area a detrital—pelitic sequence, locally about 2000 m thick, overlying a Mesozoic of Bükk facies, affected by strong tectonic deformation and dated, on the strength of deep drilling at Budafa, as corresponding to the interval between the Upper Cretaceous and the Helvetian (flyschoid?), has its northern boundary exactly coinciding with the Balaton line („The coincidence of the boundaries of the sediment-extension with the great tectonic lines is only evident in case of orogenic overthrusts", GY. KERTAI, 1961). The boreholes drilled at Buzsák [L. DUBAY, 1962] and Drávaszerdahely [V. DANK, 1962] have reached the Oligocene under Palaeozoic and Triassic formations, respectively. As observable in the lead-ore-exploring drifts of Szabadbattyán, in the course of the tectonic brecciation East-Alpine Devonian limestones must have thrusted over Lower Carboniferous deposits of Bükk facies [A. FÖLDVÁRI, 1952]. The most important evidence of the location of the Inner-Dinaric (Pennine) belt under the Austro-Alpine zone is the High Tauern and its cropping out in the Lower Engadin window [TERMIER, 1903]. Whith a view to the sequence of anchimetamorphic clay-marl shales and sandstones—conglomerates of borehole Ikervár-2, containing — as determined by J. KŐVÁRY — Upper Jurassic—Lower Cretaceous fossils, it is possible that a part of the metamorphites of the Little Hungarian Plain, adjacent to the Kőszeg—Rohonc Mts. [E. R. SCHMIDT, 1956; A. TOLLMANN, 1959; A. FAHR, 1960] is also an erosional exposure of the Pennine—Inner-Dinaric formations. Joining in STAUB's and KOBER's opinion, the Austro-Alpine, Gaetic nappe (Group *I*) of the Southern Carpathians, underlain by the so-called Danubian Autochtone (Group *II*) can also be regarded as an exposure of the Inner-Dinaric unit. This fact is — in our opinion — proved by the metamorphic character of the Upper Palaeozoic—Mesozoic formations lying on the crystalline schists of Group *II*, by the flysch facies of its Lower Cretaceous member and by the ophiolites occurring along the overthrust plane.

The *IInd tectonic line* or the „Szolnok—Ebes dislocation belt" [L. KŐRÖSSY, 1963], or the „Zagreb—Kulcs fracture" [GY. WEIN, 1970] is a first-order dislocation zone separating the Inner-Dinaric unit and the Kaposfő—Cegléd crystalline zone forming the northern edge of the Bihor Mts. Information about its character is available in southwestern Transdanubia, in the northern Trans-Tisza Region, and in the Apuseni Mts. of Transsylvania. In southwestern Transdanubia this line can be traced from the neighbourhood of Inke—Vése—Szenta up to Mezőcsokonya, on its northern side the hydrocarbon-exploratory wells have discovered, above the Palaeozoic—Mesozoic beds, a detrital—pelitic sequence of great thickness, covered for the most part by the Upper—Helvetian andesite and rhyolite volcanics already mentioned and taken earlier to be a fresh-water formation. On its southern side (Szenta, Kutas, Jákó, Kaposfő) the detrital sequence is absent and the igneous formations rest directly on the Lower Palaeozoic metamorphites. In the northern Trans-Tisza Region, from Szolnok to Debrecen, this dislocation line can be uniformly well traced. To the north of that, under the Neogene, the boreholes have reached Cretaceous—Paleogene flyschoid formations containing Jurassic limestone

reefs (and underlain by diabase and Palaeozoic rocks); to the south Lower Palaeozoic metamorphites have been cut by drilling. This latter zone was also interpreted as an overthrust line first by GY. KERTAI [1961], then by L. KŐRÖSSY [1963], too. On the basins of GY. KERTAI's cited statement it has been proved also for southwestern Transdanubia, that the „Trans-Tisza crystalline schist zone" (GY. WEIN), forming the northern thrust-sheet ranges of the *Bihor megatectonic unit, has thrusted upon the Inner-Dinaric unit covered by flyschoid formations.* The same is proved by the thrusting of the formations fo the Transsylvanian Apuseni Mts. over the flysch sequence of the Transsylvanian Metalliferous Mountains [M. ILIE, 1961].

The *IIIrd tectonical line* is the contact between the Villány belt and the northern and southern arches of the Bihor belt, along which — according to our hypothesis — the Villány belt has thrusted under the Mecsek belt.

Towards the exterior, the Austro-Alpine belt has thrusted, also along a significant dislocation line, over the Outer—Carpathian unit covered by Cretaceous—Palaeogene flysch, as demonstrated by many authors. The „Chöc" dolomite of Austro-Alpine facies could therefore have got into an Outer-Carpathian facies environment.

The structure of the *Austro-Alpine belt,* in the immediate vicinity of our country up to the Zemplén Mts. *can be classified as a double trough structure* consisting of longitudinal thrust-sheet ranges and overthrust blocks, the southern trough being represented by the Transdanubian Central Mountains and the Southern Gemerides the northern one by the zone of the northern Calcareous Alps and Northern Gemerides. The Little Hungarian Plain—Slovakian Metalliferous Mountains *metamorphi belt separating the two troughs, is a lower structural stage exposed to the erosional surface in the domed portion, which in some places* (Ikervár) *seems to have been eroded down to the Pennine unit forming the basement.* According to the present studies and to the results of the most recent refraction measurements [I. VARGA, K. VÁNDOR, GY. SÁGHI, 1967], the Rába line [V. SCHEFFER, 1948] is an outcrop of strata along a second- or third-order dislocation line rather than being a first-order dislocation belt [L. KŐRÖSSY, 1965].

Summarizing the above considerations, let us conclude that *in the Alpine-Carpathian system three down-thrusted megatectonic units* (Villány, Inner-Dinarian and Outer-Carpathian) *and two overthrusted ones* (Austro-Alpine and Bihor) can be distinguished. In the Alps and the Carpathians the Pennine windows (Tauern, Engadin, Danubian) emerging from under the Austro-Alpine belt and the Austro-Alpine „Chöc" dolomite inserted into an Outer-Carpathian facies realm, are evidence of significant nappe overthrust movements. *Within the garland of the Carpathians, the sizes of overlapping due to block-piling claim further investigations.* Considerations of crust structure [F. HORUSITZKY, 1961; E. SZÁDECZKY KARDOSS, 1970] and the structural conditions of the central mountains under study indicate that these movements *in the territory of our country cannot have reached the order of magnitude of nappe* translation movements.

Having a bilaterally symmetrical imbricated structure and characterized by block-piling, the megatectonic units of Hungary have obviously been formed simultaneously, under the same power effect.

In the territory of the under-thrusted units in the vicinity of the first-order (I, II, III) lines of dislocation the Cretaceous—Paleogene formations exhibit for the most part a flysch — flyschoid facies, being epicontinental in the overthrusted units. Since the formation of the flysch lasted from the Early Cretaceous (in some places already

from the and of the Jurassic) till Latest Palaeogene time, and since, according to K. TELEGDI ROTH's [1929] interpretation, the flysch can be regarded as „an orogenic facies on the frontal face of a dome which moved in one direction and accumulated detritus in its fore-deep", *the above structure developed continuously, beginning with the Late Cimmerian movements, in the period between the Austrian and Sava phases of the Alpine orogen.* (Should the detrital—pelitic sequence of Budafa—Inke be of a Lower Helvetian age, it might be concluded that these movements could have lasted in some places up to the Styrian phase). In the Carpathian Basin the main tectogenetic period was the Austrian phase: a fact evidenced by the hiatus and marked denudation phenomena generally observable between the Lower and Upper Cretaceous, in the East Alpine-Carpathian system (Bucegi conglomerates, Gosau series, etc.) and by the more complex structure of the Lower Cretaceous formations. which are thicker than the Upper Cretaceous. It was at this time that the Variscian masses, moving towards each other, and bounding the Tethys, brought about the present arrangement of the Alpine—Carpathian—Dinaric system. In the enviroment of the Carpathian Basin the ancient platforms hampered each-other's movement so that the territory of our country became an area of „relative pressure shadow" [F. HORUSITZKY, 1968] and was thus less affected by compression than the surrounding orogens were. The Cretaceous—Palaeogene tectogenesis, which took place in several phases — as proven by both the flyschoid sedimentation and the specific geological structure of the SW foreland of the Bakony Mts. explored by wildcatting [I. BODZAY, 1970] — was subordinate as compared to the manifestations of the Austrian folding.

In the Cretaceous—Paleogene „tectonic phases" our territory „was so greatly compressed" that „the compressed sequences, upon the subsequent geomechanical actions, already reacted as a uniform rigid consolidated mass... In this amalgamated mass mostly *fractures and fracture systems due to tensile stresses were later produced.* Young horizontal block dislocations, however,... provide evidence of *the fact that compression did not cease acting even later* [F. HORUSITZKY, 1968].

The most important event in the Neogene evolutional history of the Carpathian Basin has been the thinning and subsidence of the earth crust [L. STEGENA, 1967], supposedly due to subcrustal currents [E. SZÁDECZKY KARDOSS, 1968]. The resulting Pannonian Basin, formed in place of the earlier mountain system, has been filled up by the sediments of the Neogene archipelago.

Neogene tectonics consisted for the most part in a less intensive rejuvenation, with a lower intensity, of the Alpine fractures first of all the transversal ones. The faults and the less significant imbrications are due to „compression-bound stresses" while the graben-faults (Makó, Őrség, etc.) are connected with the subsidence of the basin. These are really beyond the scope of our study and thus have not been indicated on the maps. And the above hints at Neogene tectogenetical evolution have been given just to announce the subject to be dealt with in the next stage of this work.

CONCLUSIONS

According to the above, „the geological structure of Hungary does not represent an exotic case" strikingly differing from the Alpine-Carpathian background [F. PÁVAI VAJNA, 1930] and this „no man's land has much more Alpine and orogenetic characters than was believed before" [F. HORUSITZKY, 1961]. „The date

and causes of origin of the Alps—Carpathians and the surrounded structures can be traced back to the same circumstances" [E. R. SCHMIDT, 1961].

In the pressure shadow formed between the Variscian masses the area of the Carpathian Basin has less been compressed than the surrounding orogens [F. HORUSITZKY, 1968], and because of that „it also possesses less self—dependent characteristics than the orogenes surrounding it" [E. SZÁDECZKY KARDOSS, 1970]. The lower degree of piling is therefore — also according to our opinion — not the consequence of a more rigid behaviour of the area, but is rather due to stresses of smaller amplitude gradually reducing inwards, which would essentially correspond to the notion of the median mass, in the sense redefined by ASHGIREJ, BRUNN, JANSHIN and BELOUSOV. In the Neogene, under the less subsided area the earth crust has become thinner, and the resulting basin was inundated by the Pannonian inland sea.

The work to be done in the future is to compile an exhaustive review of what has been outlined above, and to evaluate the potential resources of oil and natural gas in a similar monograph.

SUMMARY

The Upper-Palaeozoic—Mesozoic geosyncline of the Tethys, similarly to the World-Ocean of our days was a recipient of sediments, with real oceanic depths and clearly separable facies. On the area of the Eastern Alps and the Carpathians five structural units of the crust with different facies can be differentiated which may be characterized by various intensive subsidences of the basement. Going from the North to the South these are: the Outer-Carpathian, the Austro-Alpine, the Inner-Dinarian, the Bihorian and the Villányian units. The axis of the geosyncline could be supposed on the area of the Inner-Dinarian unit in the Carbon-Triassic, while in that of the Austrian Alpine in the Jurassic. The sediment sequences of these crustal structure units have taken up the form of a folded mountain-system during the Cretaceous-Paleogene are, and they have thrusted over one another.

The area of the Carpathian Basin has become compressed less than the surrounding mountain-systems. This is not the consequence of a more rigid behaviour of the area, but is rather a result of the relative pressure shadow developed between the Variscian masses moving toward each other. In the Neogene era, under the Carpathian Basin piled up and sunk in less extent, the earth crust has become thinner and the subsidence was flooded by the Pannonian inland sea.

LIST OF SELECTED REFERENCES

ANDRUSOV, D. [1964]: Geologie der tschechoslowakischen Karpathen. Wien.

BALOGH, K. [1964]: Die geologischen Bildungen des Bükk-Gebirges. Ann. of the Hung. Geol. Inst. **48**, 245—719.

BALOGH, K. ET. AL.: Magyarázók Magyarország 200 000-es földtani térképsorozatához. Budapest.

BALOGH, K.—KŐRÖSSY, L. [1968]: Tektonische Karte Ungarns im Massstabe 1:1 000 000. Acta Geol. **12**, 255—262.

BENDEFY, I. [1966]: Contributions to the knowledge of the crustal structure of the Hungarian Basin. Acta Geol. **10**, 337—356.

CSIKY, G. [1963]*: Glubinno-sztrukturnüje i paleogeograficseszkije uszlovija oblaszti, raszpolozsennoj mezsdu rekami Dunaj i Tisza v szvete razvedki na uglevodorodü. Bull. of the Hung. Geogr. Soc. **87**, 19—36.

DANK, V. [1963]*: Stratigraphy of the Neogene basins of the Southern Alföld. Bull. of the Hung. Geol. Soc. **93**, 304—324.

DIMITRESCU, R. [1966]: Beiträge zur Kenntnis der magmatisch-tektonischen Verhältnisse im Karpatisch-balkanischen Raum. Acta Geol. **10**, 357—360.
FILJAK *et al.* [1959]*: Geology of petroleum and natural gas from the Neogene complex and its basement in the southern part of the Pannonian Basin. Nafta Zagreb, 583—598.
JUHÁSZ, Á. [1968]*: Le Flysch de Hongrie. Bull. of the Hung. Geol. Soc. **98**, 374—378.
KOBER, L. [1931]: Das alpine Europa. Berlin.
KŐRÖSSY, L. [1959]*: The flysch-like formations of the Great Hungarian basin. Bull. of the Hung. Geol. Soc. **89**, 115—127.
KŐRÖSSY, L. [1964]: Tectonics of the basin areas of Hungary. Acta Geol. **10**, 377—394.
KŐRÖSSY, L. [1965]*: Stratigraphischer und tektonischer Bau der westungarischen Becken. Bull. of the Hung. Geol. Soc. **95**, 22—36.
MAHEL, M. [1968]: Regional geology of Czechoslovakia, Praha.
MURATOV, M. V. *et al.* [1964]: Tektonika Europü. Moszkva.
MURATOV, M. V. *et al.* [1965]: Tektonika alpinszkoj oblaszti. Moskva.
NAGY, L. [1958]: A Román Népköztársaság földtana. Cluj.
ORAVECZ, J. [1964]*: Silurbildungen in Ungarn. Bull. of the Hung. Geol. Soc. **94**, 3—9.
SCHEFFER, V. [1960]: Some contributions to the geophysical knowledge of the Carpatian basins. Acta Technica. **30**, 423—461.
SCHEFFER, V. [1955]*: Regionale geophysikalische Übersicht des Grenzgebietes der Ostalpen. Bull. of the Hung. Geol. Soc. **95**, 5—21.
SCHMIDT, E. R. [1957]: Geomechanika. Budapest.
SIKOSEK *et al.* [1967]: The genetical problems of Dinarids. Carpatho-Balkan Geol. Ass. VIIIth Congr. Beograd.
STEGENA, L. [1964]: The structure of the earth's crust in Hungary. Acta Geol. **8**, 413—431.
STEGENA, L. [1967]*: On the formation of the Hungarian Basin. Bull. of the Hung. Geol. Soc. **97**, 278—285.
STEVANOVIC, P. [1967]: Geological review of the Carpatho-Balkanides of Yugoslavia. Carpatho-Balkan Geol. Ass. VIIIth Congr. Beograd.
STILLE, H. [1953]: Der geotektonische Werdegang der Karpathen. Beitr. Geol. Jahrb. **8**, Hannover.
SZALAI, T. [1958]: Geotektonische Synthese der Karpaten. Geof. Közl. **7**, 111—145.
SZALAI, T. [1970]: Die Pannonische Masse (Tisia). Acta Geol. **14**, 71—82.
SZÁDECZKY-KARDOSS, E. [1967]: A map of geological evolution of South-Eastern Europe. Acta Geol. **11**, 187—203.
SZÁDECZKY-KARDOSS, E. [1968]: A Föld szerkezete és fejlődése. Budapest.
SZÉNÁS, GY. [1969]: The evolution and structure of the Carpathian Basin. IXth Session of the Carpatho-Balkan Geol. Ass. Budapest.
TELEGDI-ROTH, K. [1929]: Magyarország geológiája. Budapest.
UHLIG, V. [1907]: Tektonik der Karpathen. Sitzungsb. Akad. Wien. Mat. Naturw. Kl.
VADÁSZ, E. [1954]: Magyarország földtani szerkezeti vázlata. Comm. of the Hung. Acad. of Sci. **14**, 217—255.
VADÁSZ, E. [1960]: Magyarország földtana. Budapest.
WEIN, GY. [1969]: Tectonic review of the Neogen-covered areas of Hungary. Acta Geol. **13**, 399—436.

Beside the above references the writers have made use of the papers presented by AL. CODARCEA, C. GHEORGHIU, F. HORUSITZKY, M. ILIE, GY. KERTAI, H. KÜPPER, M. MAHEL, M. MÉSZÁROS, D. MURGEANU, G. PANTÓ, D. PATRULIUS, K. PETKOVIC, E. R. SCHMIDT, V. I. SLAVIN and O. S. VIALOV to the International Conference on Mesozoic Stratigraphy, Budapest 1959 (Ann. of the Hung, Geol. Inst. Vol. *49*): of the official reports of the Hungarian National Oil-and-Gas Trust, and of partly unpublished contributions to petroleum geology by E. BALÁCS, K. BALLA, I. BÉRCZINÉ, I. BODZAY, G. CSIKY, CSONGRÁDINÉ, V. DANK, L. DUBAY, L. FACSINAY, L. GRÁF, Á. JUHÁSZ, GY. KERTAI, Á. KOCSIS, K. KORIM, J. KÓKAY, G. KOVÁCS, A. KŐHÁTI, J. KŐVÁRY, L. KŐRÖSSY, E. KRIVÁN—HUTTER, L. MAJZON, K. MAKKAI, M. R. NYIRŐ, S. PAPP, V. SCHEFFER, L. STRAUSZ, GY. SZALÁNCZY, M. SZÉLES, K. SZEPESHÁZY, G. SZUROVY, J. TOMOR, I. VARGA, R. VÁNDORFI, GY. VECSERNYÉS and L. VÖLGYI.

The asterisked (*) references are titles of foreign-language summaries of the respective items. In Hungarian-language publications only these titles have been indicated wherever such were available.

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REMARKS ON THE THERMAL INVESTIGATION OF SEDIMENTARY ROCKS CONTAINING ORGANIC MATERIAL

GY. GRASSELLY and MRS. M. AGÓCS

INTRODUCTION

In the investigation of sedimentary rocks containing clay minerals and carbonates, the determination of the amount and character of organic material present cannot be neglected. It seems to be essential to identify the organic components soluble in organic solvents as well as the insoluble ones especially from the point of view of hydrocarbon researches. Here it is not aimed to deal with the possibilities of instrumental investigations of separation and qualitative or quantitative determinations of different organic components present in the sediments, merely the question will be dealt with what kind of conclusions may be drawn from the character and position of exothermic peaks originated from the organic material and the DTA curves of sedimentary rocks and to what extent may these exothermic effects be used to the (at least qualitative) characterization of organic material present.

It is well known that the thermal effects of clay minerals are interfered by thermal effects from the combustion processes of the organic material since — without applying an inert atmosphere — the strong exothermic effect due to the combustion of the organic material is in the same temperature interval as the strong endothermic effect of clay minerals, first of all that of kandites.

The investigations were carried out with a „Derivatograph" constructed by PAULIK, F., PAULIK, J. and ERDEY, L. which renders possible to trace and record simultaneously *T*, *TG*, *DTG* and *DTA* curves.

Forms of appearance of organic material in sediments

According to HUNT and JAMIESON [1956] as well as HUNT and FORSMAN [1958] and other authors in the non-reservoir rocks the organic material may be present mainly in two forms:

a) organic compounds soluble in organic solvents as the paraffines, naphtenes and other N-S-O-containing organic compounds similar in composition to the heavier fraction of oil to be found in the reservoir rocks as well as the soluble bituminous components similar to those of the oil;

b) an insoluble organic material, the kerogen.

Samples of Lower Pannonian sedimentary rocks investigated are derived from the Algyő oil-field (near Szeged) and most of them contain organic material in some form if in fairly varying and small amounts as shown by chemical and DTA investigations. The petrographical investigation of thin sections of these rocks also show-

ed the presence of coalified plant remnants, some lignite and of remains of oil dried in the pores. Therefore it seemed to be purposeful to study the effect of combustion processes of different kinds of organic material exerted on the DTA curves.

General features of thermal effects of organic materials

The exothermic effect due to the combustion of the organic matter appears as a rule between 300—600 °C with a maximum at about 400° C the temperature of which, however, may be changed depending on the character of the organic material. The temperature of exothermic peaks characteristic of different coaly material (if the rock contains the given material in 5 per cent) is given by GRIMSHAW and ROBERTS [1957]. Thus, the temperature of the exothermic peak is at 389° C in the case of lignite, the temperature of the 1. exothermic peak is at 387° C and 485° C for the 2. exothermic peak in the case of oil shale whereas the first exothermic peak appears at 390° C in the case of bituminous coals. The position of this peak is independent either a low or middle or high rank bituminous coal is in question. The temperature of the second exothermic peak, however, increases in this series from 515° C to 524° C though this change is not a significant one.

From the point of view of thermal investigations the ratio of volatile and non-volatile carbon proves to be interesting and essential. The ratio of non-volatile carbon to the total carbon in oil shales and lignite amounts to 35% and 54%, respectively, depending on whether they contain a significant amount of components richer in carboxyl- and hydroxyl-groups, while the amount of non-volatile carbon reaches 85 per cent and 96 per cent, respectively, in the bituminous coals and the anthracite.

The shift of ratio of volatile and non-volatile carbon exerts an essential influence on the temperature of the exothermic peak of the DTA curve, namely, the first peak appearing between 350—390° C may be taken as originated from organic compounds richer in hydroxyl- or other oxygen-containing groups whereas the second exothermic peak at higher temperatures represents the combustion of non-volatile carbon and at an even higher temperature occurs the combustion of elemental carbon. E. g. according to GRIMSHAW and ROBERTS [1957] the temperature of the exothermic peak is at 564° C in the case of anthracite and 613° C of graphite.

EXPERIMENTAL PART

Types of exothermic peaks in the DTA curves of samples investigated

While examining the character of exothermic peaks between 300—520° C on derivatograms of Lower-Pannonian sedimentary rock samples from Algyő some types of peaks may be distinguished emphasizing, however, that the single types don't mean a sharp separation, there exists a transition between the single types. The exothermic peak of *type 1* is characterized by the appearence at about 395—415° C of a well developed inflection instead of an expressed exothermic peak of lower temperature whereas the temperature of the 2nd well developed and dominant exothermic peak is at about 490—515° C.

The exothermic peak of *type 2* differs from the former essentially merely in the peak temperature and the *1* and 2 exothermic effects are more balanced. The first peak is at 350—375° C and the second — of similar intensity — at 470—475° C. The temperature of the peaks is in connection with the amount and the fineness of

distribution of organic material present. The lower is the concentration the lower will be the peak temperature.

The peak of *type 1 (Fig. 1)* is registered on the DTA curve of a sample containing 3,15% organic material whereas that of the sample showing a peak of *type 2* only 0,75%.

In the case of peaks of *type 3* hardly any difference between the first and second exothermic effects can be stated. An exothermic effect reveals from 365° C to 475 °C.

The peak of *type 4* is essentially the contrary to type 2, namely, the first peak between 340—375° C is more expressed whereas the second one between 470—495° C is rather weak or sometimes hardly observable.

The organic matter content of a sample showing in its derivatogram a peak of type 3 was 0,92% and 0,87% of a sample showing on its DTA curve a peak of type 4.

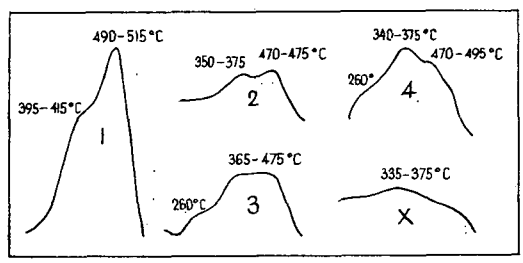

Fig. 1. Types of the exothermic DTA peaks originated by the organic material content of the samples.

Considering the frequency of exotherm peaks of various types peaks of type 3 and 4 proved to be the most frequent. Peaks of type 1 and 2 could be observed only on DTA curves of relatively few samples.

The question may arise whether or not is possible to draw some conclusions by model-experiments from the character of exothermic peaks on DTA curves of sediments containing organic material on the organic material present, taken as known the fact that the exothermic effect of lower temperature belongs to the combustion processes of organic components of higher volatility and the exothermic effect of higher temperature represents the combustion of components of lower volatility and the „fixed" carbon.

Thermal effects of organic materials extractable in organic solvents

Starting from the consideration that the samples investigated may contain soluble organic material similar to components of heavier fraction of oil — even more since the samples are derived from reservoir rocks — examinations were carried out concerning the effect of the oil and its single fraction, respectively, on the character of exothermic peaks observable on the DTA curves.

An oil sample from the Deszk-field was mixed in 5 per cent to Al_2O_3 and the derivatogram (T, TG, DTG, DTA) was taken, as shown in *Fig. 2.*

The very weak exothermic effect on the DTA curve at 150° C is probably in connection with components of higher volatility, followed by well developed exothermic peaks at 350 and 390° C, respectively and at last a well pronounced inflection may be registered at 500° C. The main maximum on the DTG curve is at 310° C (the first very weak maximum is at 70 °C) and the elongated very flat maximum on

the DTG curve at about 500° C points to a process following the main reaction. The step on the TG curve, corresponding to the main reaction is between 150 and 420° C and the maximum of loss of weight is also in this temperature interval. The beginning and the end of the step on the TG curve is determined by the corresponding minima of the DTG curve.

In the described exothermic effect the complex effect of single fractions of oil is revealed, therefore, to study the single fractions on the DTA etc. curves, the oil sample was separated to six fractions by fractional destillation at atmospheric pressure.

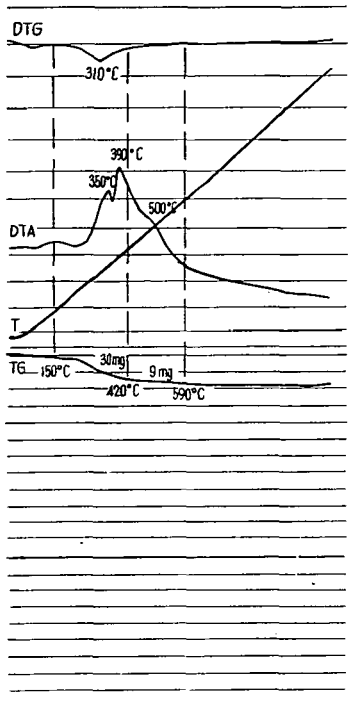

Fig. 2. Derivatogram of oil sample from Deszk (5 per cent oil soaked in Al_2O_3)

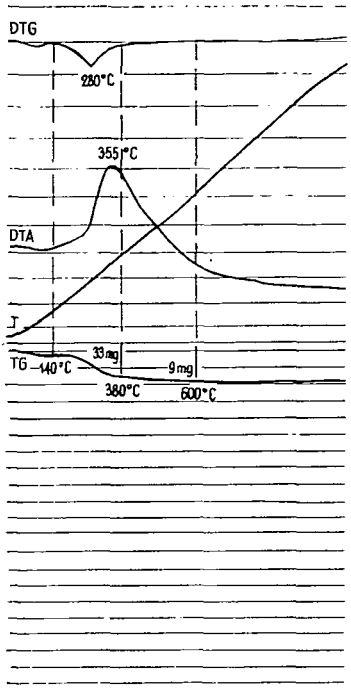

Fig. 3. Derivatogram of oil fraction distilled between 280—300° C (5 per cent in Al_2O_3)

TABLE I.

No. of fractions	Distillation temperature interval	Per cent	Remarks
1	—100	20,40	
2	100—200	8,65	
3	200—280	19,35	
4	280—300	21,75	
5	300—350	21,10	
6	350—	8,75	Dist. residue

To compare the effect of single fractions to that of the oil sample, 5—5 per cent from fractions 4 and 6 were mixed to Al_2O_3. Their derivatogram is shown in *Fig. 3* and *4*.

Furthermore, a rock sample of relatively low (0,9 per cent) organic material content was chosen and of the oil fractions mentioned in Table I fractions No 3, 4, 5, and 6 were mixed to it in 0,5 and 3 per cent, respectively. In *Figs. 5—8* are shown only mixtures containing 3 per cent of the fractions mentioned.

In general the following tendencies may be stated:

1. The maximum on the DTG curve preceded the temperature of the maximum (exothermic peak) on the DTA curve in the case of the different fractions and the most pronounced loss of weight on the TG curve belongs to this DTG maximum.

TABLE II

Beginning and end of TG steps belonging to the DTG maximum	Distillation temperature of the fractions
60—325° C	200—280° C
115—345° C	280—300
100—355° C	300—350
180—400° C	350° C

TABLE III

Distillation temperature °C	Amount of fraction in the rock sample per cent	Temperature of the DTG maximum °C
200—280	0,5	180
	1,0	
	3,0	200
280—300	0,5	230
	1,0	240
	3,0	260
300—350	0,5	240
	1,0	250
	3,0	290
350—	0,5	300
	1,0	310
	3,0	340

2. The temperature of the maximum on the DTG curve approaches more and more to the temperature of the exothermic effect on the DTA curve if fractions of higher boiling point and greater C-number are present. The higher is the distillation temperature of the fraction the higher is the temperature of the DTG maximum as shown in *Fig. 9.*

3. The temperature of the beginning and end of steps on the TG curve belonging to the loss of weight of the reaction indicated by the DTG maximum is also

influenced by the boiling point of the fraction. Higher boiling point, greater C number means the shift of this step to higher temperatures.

4. The temperature of the DTG maximum is influenced not only by the boiling point and composition of the fractions but also by the amount of the fractions.

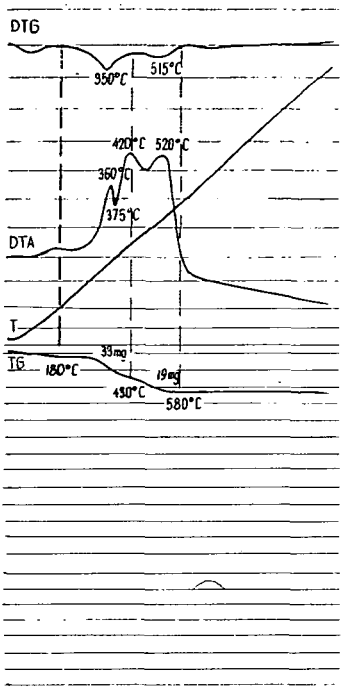

Fig. 4. Derivatogram of the oil distillation residue (after distillation at 350° C; 5 per cent in Al_2O_3)

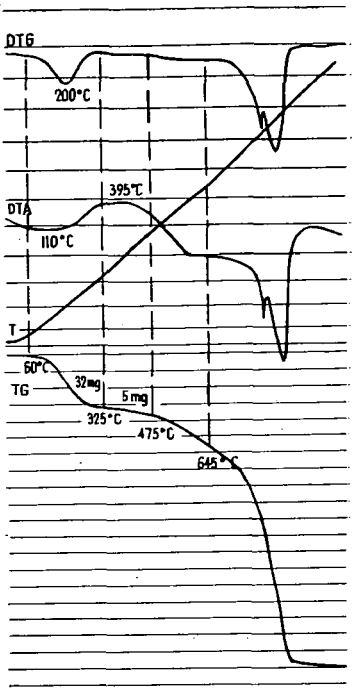

Fig. 5. Derivatogram of a sedimentary rock sample containing 3 per cent of oil fraction distilled between 200—280° C

weighed in. The lower is the temperature of the DTG maximum the smaller is within the same fraction the sample weighed in.

5. Similary, the temperature of the main exothermic peak on the DTA curve rises by increasing the boiling point and the amount of fraction present as shown in *Fig. 10* in the case of distillation residue, fraction 6.

The temperature of the DTA maximum in the case of fraction No 4 (distillation temperature interval 280—300° C) also increases corresponding to the increasing amount (0,5, 1,0 and 3,0 per cent) of the fraction present *i. e.* the peak temperature is 370—380—425° C.

6. Comparing the exothermic effects derived from the combustion at a higher temperature of components in derivatograms shown in *Fig. 4* and *8* the mutual interference of the organic material and clay minerals is striking. *Fig. 4* shows the derivatogram of Al_2O_3 with 5 per cent oil distillation residue (the residue after distillation at 350° C) and *Fig. 8* the derivatogram of a rock sample containing some clay mineral and 3 per cent of the same oil fraction. On the derivatogram of the

rock sample the exothermic effect of higher temperature deriving from the distillation residue appears merely as a not well defined inflection at about 500° C.

Comparing derivatograms of *Figs. 2, 3* and *4* the DTG maximum on the derivatogram of the original oil sample *(Fig. 2)* is at 310° C, in the case of distillation fraction No 4 at 280° C *(Fig. 3)* and at last at 350° C on the derivatogram of the distillation residue *(Fig. 4)*. In the exothermic effect of the original oil sample the common effects of components of lower and higher boiling point appear. According to Table I, however, in the original oil sample fraction No 6 amounts to merely

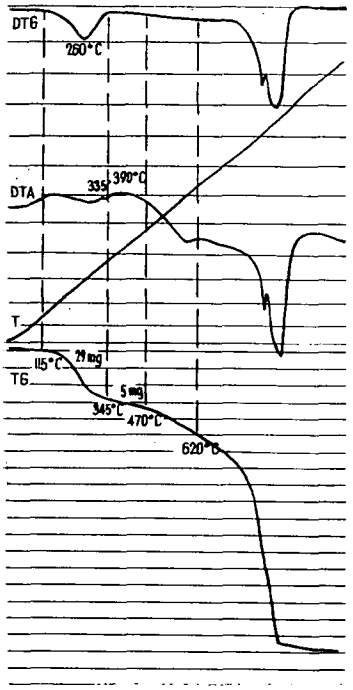

Fig. 6. Derivatogram of a sedimentary rock sample containing 3 per cent oil fraction distilled between 280—300° C

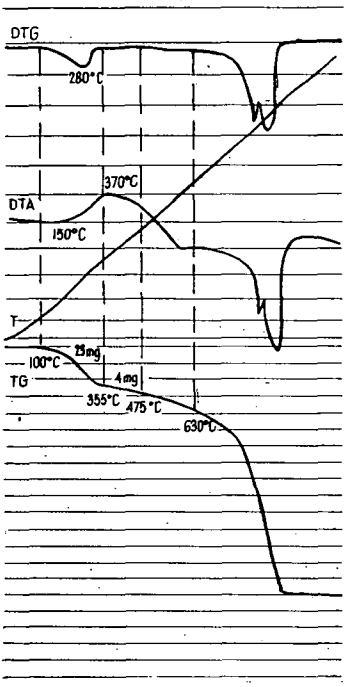

Fig. 7. Derivatogram of a sedimentary rock sample containing 3 per cent oil fraction distilled between 300—350° C

8,75 per cent, hence, the exothermic effect attributable to this fraction at 500° C appears only as a weak inflection. On the contrary, on the derivatogram of fraction No 6 a further well developed exothermic effect appears at 515° C which could hardly be observed on the derivatogram of the original oil sample at 500° C and did not appear on the derivatogram of the lower fractions. The increasing ratio of components of higher boiling point involves that the loss of weight measurable on the TG curve becomes more considerable also in a higher temperature interval (430—580° C) whereas in the case of fractions of lower boiling point the loss of weight is dominant in a lower temperature interval (60—400° C).

Remarks mentioned above may promote at least the qualitative interpretation of exothermic effects appearing on the derivatogram of sedimentary rocks containing soluble hydrocarbons, however, the thermal effect of the insoluble organic matter cannot either be neglected.

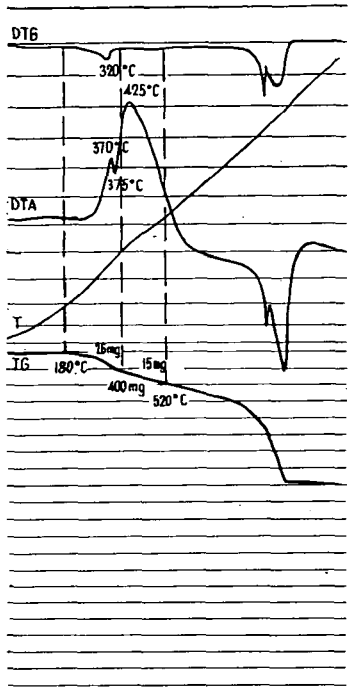

Fig. 8. Derivatogram of a sedimentary rock sample containing 3 per cent distillation residue

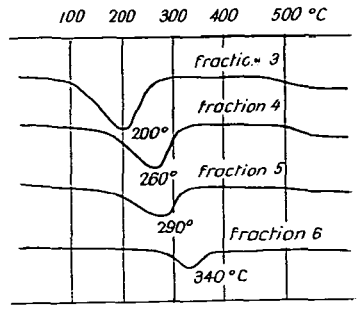

Fig. 9. Shift of the DTG maxima in the case of the successive distillation fractions

Thermal effects of insoluble organic materials (kerogen, lignite)

From one of our samples relatively rich in organic matter after extracting the soluble organic compounds, kerogen was isolated according to the method proposed by FORSMAN and HUNT [1958]. The organic carbon content of the sample amounted to 2,60 per cent corresponding to 3,15 per cent total organic material, after having been multiplied by 1,21, the organic factor calculated by the authors mentioned.

The *C/H* ratio of the kerogen isolated from the sample proved to be 14,3, very close to that of the fine kerogen fraction of the Wilcox-shale (14,7) as it is given the paper of FORSMAN and HUNT. For the sake of comparison, the *C/H* ratio in the oil fraction No 6, *i. e.* in the residue after distillation at 350° C, was 7,4.

The derivatogram of the kerogen isolated is shown in *Fig. 11.*

The similarity on the DTA curve between the character of the exothermic effect of the kerogen sample and the exothermic peak of type 1 observed on the derivatogram of the different original rock samples is striking. A very little difference

can, however, be stated, namely, on the DTA curve of the isolated kerogen a definite inflexion appears at about 360° C and the maximum of the peak is at 470° C whereas on the derivatogram of the original sample — from which the kerogen was isolated — the inflexion is at 395° C and the peak maximum at 510° C. In the case of the isolated kerogen the maximum on the DTG curve, attributable to the organic material, is at 445° C, and in the case of the original sample at 480° C. On the TG curve the main step corresponding to the loss of weight is between 280—525° C in the case of kerogen, and between 270—380° C in the case of the original rock sample.

If only 5 per cent kerogen was mixed to the rock sample, the inflexion on the DTA curve appears also at 360° C (as in the presence of 10 per cent kerogen) the peak maximum is somewhat lower: at 460° C, the DTG maximum at 440° C and the main loss of weight step in the TG curve is between 280—520° C i. e. a little lower than in the case of 10 per cent kerogen + 90 per cent Al_2O_3 mixture.

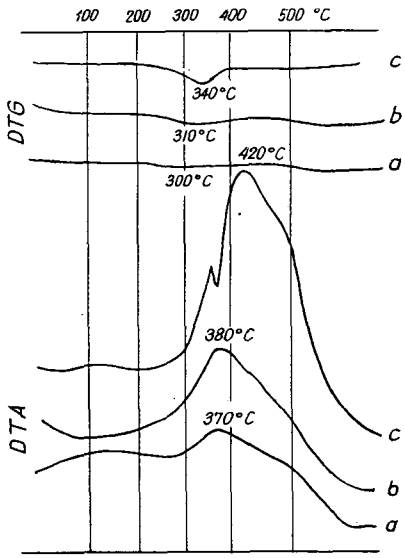

Fig. 10. DTA and DTG effects of the oil distillation residue mixed to rock sample if the residue amounts to *a)* 0,5 per cent; *b)* 1 per cent and *c)* 3 per cent

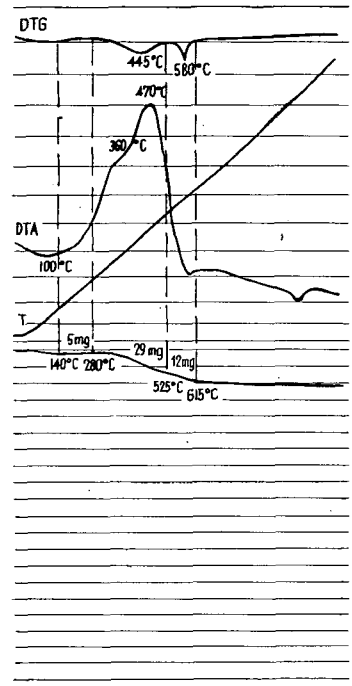

Fig. 11. Derivatogram of kerogen isolated from Lower Pannonian sandstone (10 per cent kerogen in Al_2O_3)

For information on the effect of coaly remnants on the derivatogram under the conditions of the investigations applied, 5 per cent lignit powder was mixed to Al_2O_3 and 10 per cent to a rock sample relatively poor in organic material. The derivatograms are shown in *Figs. 12* and *13*.

In the course of thermal investigations of coals, WELTNER [1965] as well as BÁTOR and WELTNER [1965] stated that on the DTG curve two maxima appear,

the lower temperature maximum above 200° C corresponds to the combustion processes of compounds of higher volatility and the higher maximum at about 350—400° C can be attributed to the combustion of the components of lower volatility + the „fixed" carbon. According ot the authors mentioned, the greater the grade of coalification the lower the first effect and more expressed the second peak of higher tem-

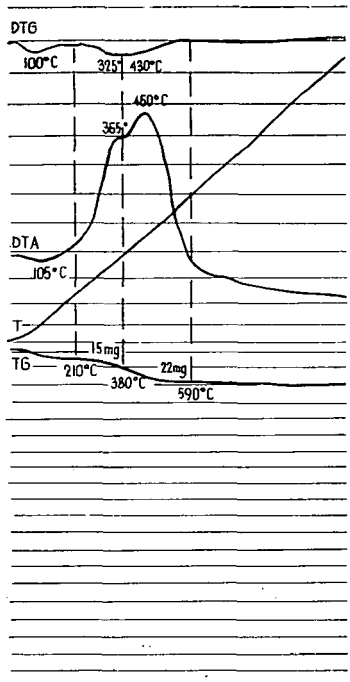

Fig. 12. Derivatogram of lignite (5 per cent in Al_2O_3)

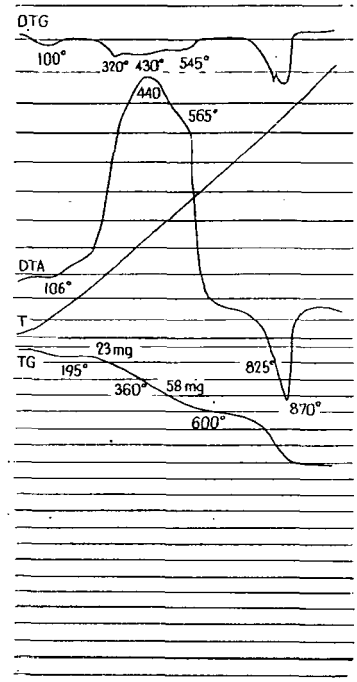

Fig. 13. Derivatogram of lignite (10 per cent in a rock sample)

perature whereas at a lower degree of coalification the first effect seems to be more intensive. This remark concerning the DTG maxima totally agrees with the statement of GRIMSHAW and ROBERTS referred previously. According to these authors the exothermic peak on the DTA curve appears at 390° C in the case of lignite whereas the DTA curve of bituminous coals shows two exothermic peaks; the first at 390° C and the second at 500° C. As the volatile content increases *i. e.* in the case of high rank coals towards the direction anthracite—graphite the first effect disappears and the intensity of the second peak of higher temperature will be dominating.

It is to be added that the peak-temperature is influenced not only by the ratio of components of higher or lower volatility but also by the amount of the components present as shown in *Figs. 9* and *10*.

Comparing the derivatograms of kerogen isolated and the lignite the following statement may be drawn:

1. The type of the DTA effect is the same and corresponds to the exothermic peak of type 1 *(Fig. 1)*.

2. The DTG curve of the kerogen shows only one maximum at about 440—445° C whereas on the DTG curve of the lignite disregarding the maximum at 100° C two maxima appear at 320—325° C and 420—430° C originated by overlapping reactions.

3. Corresponding to the one DTG maximum, the main loss of weight step on the TG curve is between 280—525° C in the case of kerogen whereas in that of the lignite two steps may be distinguished on the TG curve corresponding to the double DTG maxima, the first between 210—380° C and the second between 380—590° C and the latter means the greater loss of

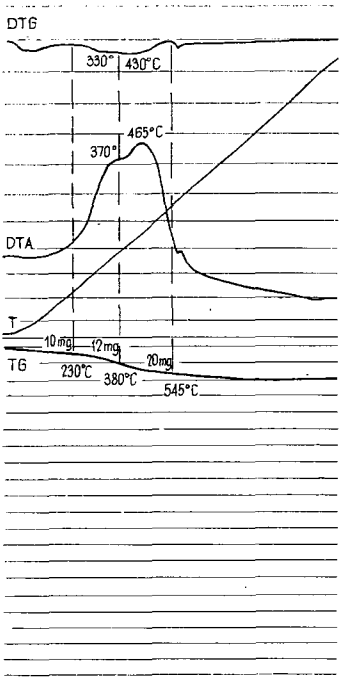

Fig. 14. Derivatogram of a mixture of 2,5 per cent kerogen — 2,5 per cent lignite — 95 per cent Al_2O_3

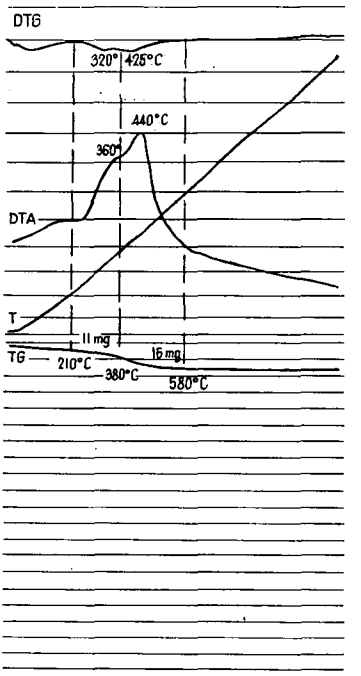

Fig. 15. Derivatogram of a mixture of 1 per cent kerogen — 3 per cent lignite — 96 per cent Al_2O_3

weight. In the presence of clay minerals, however, this second step originated by the combustion of organic material cannot agreably be distinguished by the overlapping step originated by the decomposition of the clay minerals as in the presence of organic material and clay minerals both the exothermic effect of the organic material and the following endothermic effect of the clay minerals on the DTA curve will also be distorted *(Fig. 13)* and on the DTG curve after the maximum at 320 °C and 420 °C another maximum appears at 545 °C attributable to the decomposition of the clay minerals and partly overlapping the second maximum.

Thermal effects in joint presence of different organic substances

Derivatograms of mixtures of kerogen — lignite and oil—lignite (all the components mixed to Al_2O_3 in various ratios) were also studied as shown in *Figs. 14—17.* Considering the derivatograms the following statements can be established.

1. On the DTG curve of different mixtures in the presence of lignite its characteristic two maxima appear at 300—330° C and at 420—440° C, respectively, disregarding whether oil or kerogen was the other component beside lignite.

2. The exothermic DTA effect on the derivatogram of the kerogen — lignite mixtures corresponds to the peak of type 1, and the temperature of the DTA and DTG maxima is influenced by the kerogen/lignite ratio, by decreasing the kerogen content the temperature of both maxima will somewhat be lowered.

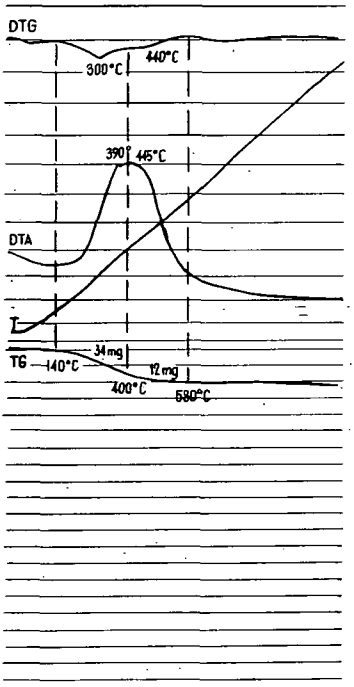

Fig. 16. Derivatogram of a mixture of 4 per cent oil — 1 per cent lignite — 95 per cent Al_2O_3

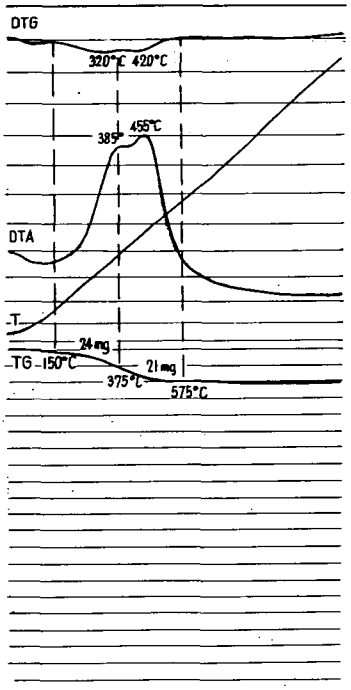

Fig. 17. Derivatogram of a mixture of 2,5 per cent oil — 2,5 per cent lignite — 95 per cent Al_2O_3

3. In connection with the two DTG maxima originated by overlapping reactions as mentioned in the case of pure lignite, the loss of weight represented by the TG curve can also be divided into two steps, the first starts at 210—230° C and the second from 380° C and ends at 545—580° C. The relatively greater loss of weight is represented by the second step at higher temperature pointing to that the components of lower volatility + the „fixed" carbon play a greater role than the highly volatile components.

While interpreting the exothermic effects of kerogen-lignite mixtures the following are to be taken into consideration:

It is mentioned by FORSMAN [1963] in his paper dealing with the geochemistry of kerogen that generally three types of kerogen can be distinguished on the basis of investigating its oxidation processes. The first type of kerogen resembles of humic material playing a role in lignites, peats, and coals, too, the second type may be taken of algal origin whereas the origin of the third type is questionable, however, in the course of pyrolysis this type also produces oil.

On the basis of the great similarity of the DTA effects of the lignite sample investigated and the kerogen isolated from the rock sample, disregarding the differences in peak temperatures, it may be supposed that the kerogen investigated may be considered as belonging to the first type according to FORSMAN's grouping.

According to BREGER and WHITEHEAD [1951] the degradation of the lignin is indicated by the intensive exothermic peak at 425° C. On examining the derivatograms of lignite or kerogen or mixtures of the two components it may be stated that the peak temperature is shifted towards higher temperatures in the presence of kerogen. This fact may presumably be interpreted that the devolatilization of the humic matter occurs and compounds of higher stability are formed by polymerisation or condensation or such are already present in the kerogen, the degradation of which occurs only at higher temperature.

4. In the case of oil and lignite mixtures by decreasing the oil ratio rather the exothermic peak of type 2 appears whereas by increasing the amount of oil relating at least to the amount of lignite, the difference between the two peaks in the exothermic DTA effect nearly totally disappears thus the effect will be very similar to the peak of type 3.

5. On the DTG curve of oil-lignite mixtures also two maxima appear at 300—320° C and 420—440° C, respectively, as a result of succeeding and partly overlapping reactions. By increasing the oil ratio the first reaction and the DTG maximum corresponding to it will be more expressed, consequently, the loss of weight recorded by the step on the TG curve between 140—400° C will be dominating. (The derivatogram of the oil used is shown in *Fig. 2*) The loss of weight in the temperature interval mentioned may be attributed to the components combustible at a lower temperature, introduced into the mixture in a greater amount by adding oil to it. By decreasing the oil ratio the two maxima on the DTG curve will be more balanced and the two steps on the TG curve at 150—375° C 375—575° C approach each other.

SUMMARY

a) On the derivatogram of the kerogen only one DTG maximum appears, on the other hand, on the DTA curve the main exothermic effect appears at 460—475° C after the inflection at 350° C. The main step on the TG curve, corresponding to the loss of weight, occupies the smallest temperature interval from 280° C till 500—525° C among all materials and mixtures investigated.

b) It is characteristic of lignite that two DTG maxima can be observed disregarding the maximum at about 100° C due to dehydration; the maximum of lower temperature is at 320—325° C, the other one of higher temperature at 420—430° C somewhat lower than the single maximum of kerogen. Corresponding to the double DTG maxima, on the TG curve two definite steps can be distinguished covering together a greater temperature interval than in the case of kerogen. The loss of weight starts already at about 195—210° C and the second step begins at 360—380° C and terminates at 590—605° C. The character of the exothermic effect on the DTA

curve is similar to that of the kerogen isolated by the authors at least in the case of the lignite sample used for comparison. The inflexion point is at 365—375° C as in the exothermic effect of the kerogen, the temperature of the main exothermic peak is somewhat lower, 440—450° C.

c) Considering the derivatogram of the oil sample a pronounced DTG maximum can be observed at an essentially lower temperature (310° C) than that of the kerogen, however, nearly equals with the temperature of the lower temperature DTG maximum of the lignite. The loss of weight step starts at an essentially lower temperature than with kerogen and lignite, at about 140—150° C pointing to the loss of lower boiling point components of the oil. Corresponding to the heavier, bituminous components of the oil, an observable second DTG maximum also appears and in connection with it a second step on the TG curve pointing to the very small loss of weight can also be observed. This second step on the TG curve and the DTG maximum, respectively, appear definitely merely on the derivatogram of the distillation residue of the oil (residue after distillation at 350° C). Its derivatogram shows already two pronounced DTG maxima at 350° C and 515° C.

d) Kerogen being present beside the lignite and oil beside lignite, respectively the main characteristics of these components as summarized above are reflected together on the derivatogram depending upon the quantitative relations. It is characteristic in the presence of oil that the step on the TG curve starts at a lower temperature than in the case of pure lignite or kerogen, hence, the first DTG maximum appears also at a lower temperature, thus, if a step of considerable loss of weight starts already at 200°C on the derivatogram of a sedimentary rock, the presence of oil traces may be supposed and if a second step can be observed on the TG curve and correspondingly two DTG maxima and the second TG step ends above 550—570°C, the presence of lignite can presumably be considered.

From the model-experiments outlined it may be concluded that by the differential thermal analysis of sedimentary rocks containing organic matter, the comparison of the character and temperature of effects appearing on the DTA and DTG curves as well the steps on the TG curves render possible to approach at least qualitatively the character of the organic material present.

REFERENCES

BÁTOR, B., WELTNER, M. [1965]: Investigation of reactivity of coals. — Magyar Kémiai Folyóirat **71**, 329—333.

BREGER, I. A., WHITEHEAD, W. L. [1951]: Lignin in coal genesis. — Fuel, London, **30**, 247—253.

FORSMAN, J. P. [1963]: Geochemistry of kerogen. — In: Organic Geochemistry. Edited by J. BREGER, Pergamon Press.

FORSMAN, J. P., HUNT, J. M. [1958]: Insoluble organic matter (kerogen) in sedimentary rocks. Geochim. et Cosmochim. Acta **15**, 170—182.

GRIMSHAW, R. M., ROBERTS, A. L. [1957]: Carbonaceous materials. — In: The differential thermal investigations of clays. Edited by R. MACKENZIE, Mineralogical Society of London.

HUNT, J. M., JAMIESON, G. W. [1956]: Oil and organic matter in source rocks of petroleum. — Bull. Amer. Ass. Petrol. Geol., **40**, 477—488.

WELTNER, M. [1965]: Derivatographic investigation of oxidation by hydrogene hyperoxide of the lignite from Várpalota. — Magyar Kémiai Folyóirat **71**, 194—198.

WELTNER, M. [1965]: Derivatographic investigations of combustion process of coals. — Magyar Kémiai Folyóirat **71**, 316—318.

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INVESTIGATION OF SPORES AND POLLEN GRAINS OF THE CARBONATE MANGANESE ORE BORE SAMPLES FROM ÚRKÚT

M. KEDVES, P. SIMONCSICS

INTRODUCTION

It is proved by our earlier publications [SIMONCSICS and KEDVES 1961, 1969, KEDVES and SIMONCSICS 1964 *a, b*] that the sedimentary manganese ore from Úrkút, particularly the carbonate ore, is rich in microfossils. We investigated and described the sporomorphs of two profiles. In the profile of Shaft III of Úrkút we have differentiated three layers on the basis of the quantitative occurrence of spores and pollen as well as of plankton remains (lower, *A* layer: *Classopollis* layer; middle, *B* layer: *Crassophaeridae* layer; upper, *C* layer: *Spheripollenites* layer). Overmore, we have tried to reconstruct the riverside zonation of vegetation.

The aim of the present investigations is:

a) To prove the flora components known hitherto, completing them with possible new ones from among the samples of the more than 100 m profile,

b) to ascertain the spore and pollen communities by means of a quantitative analysis of the new samples,

c) to class the company-complexes in layers and compare them to earlier results.

MATERIAL AND METHOD

The layer profile of boring 316 at Úrkút was at our disposal from 210,0 m till 106,2 m. The sampling is unfortunately not continuous. The object of our investigations was formed by twenty samples of the approximately 100 m thick layer, being 0.1, 0.2, 0.3, 0.8 and 1.0 m thick each.

We explored the single samples in averages, as well as — in case of samples suitable for that — disconnecting the single samples to more homogeneous strips. The strips were of light brown and greenish-brown colour according to the degree of oxidation of the manganese content.

In the course of the microscopic investigations we have striven for getting full details concerning the qualitative analysis, and endeavoured to take on a diagram the quantitative data summing them up according to facies-ecological, microstratigraphic purposes.

RESULTS

A) Data of the qualitative analysis:

Fgen.: *Leiotriletes* [NAUMOVA 1937] R. POT. and KR. 1954.

1. *L. manganicus* KDS. et SICS. 1964 a

2. *L. urkutensis* KDS. et SICS. 1964 a
3. *L. sphagnoides* KDS. et SICS. 1964 a
4. *L. transdanubicus* KDS. et SICS. 1964 a
5. *L. pflugi* SICS. et KDS. 1961
L. pflugi SICS. et KDS. 1961 fvar. *triplan* SICS. et KDS. 1961.

Fgen: *Punctatisporites* IBRAHIM 1933
1. *P. krutzschi* KDS. et SICS. 1964 a
2. *P. goczani* KDS. et SICS. 1964 a
3. *P. circulus* KDS. et SICS. 1964 a
4. *P. parvigranulatus* LESCHIK 1955

Fgen.: *Sphagnumsporites* RAATZ 1937.
1. *Sp. psilatus* [ROSS 1949] COUPER 1958
2. *Sp. clavus* [BALME 1957] DE JERSEY 1959

Fgen.: *Toroisporis* W. KR. 1959

Subfgen.: *Toroisporis (Toroisporis)*
1. *T. (Toroisporis) crassiexinus* KDS. et SICS. 1964 a
2. *T. (Toroisporis) crassitorus* KDS. et SICS. 1964 a
3. *T. (Toroisporis) toralis* [LESCHIK 1955] KDS. et SICS. 1964 a
4. *T. (Toroisporis) macrosinus* KDS. et SICS. 1964 a
5. *T. (Toroisporis) rectitorus* KDS. et SICS. 1964 a
6. *T. (Toroisporis) curvitorus* KDS. et SICS. 1964 a
7. *T. (Toroisporis) hungaricus* KDS. et SICS. 1964 a

Subfgen.: *Toroisporis (Toripunctisporis* W. KR. 1959)
1. *Toroisporis (Toripunctisporis) hungaricus* n. fsp.
(Table I, 1, 2, Fig. 1)

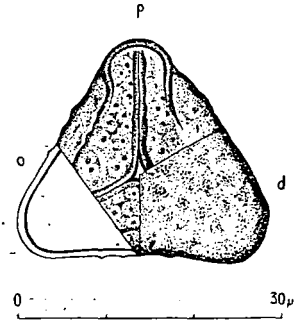
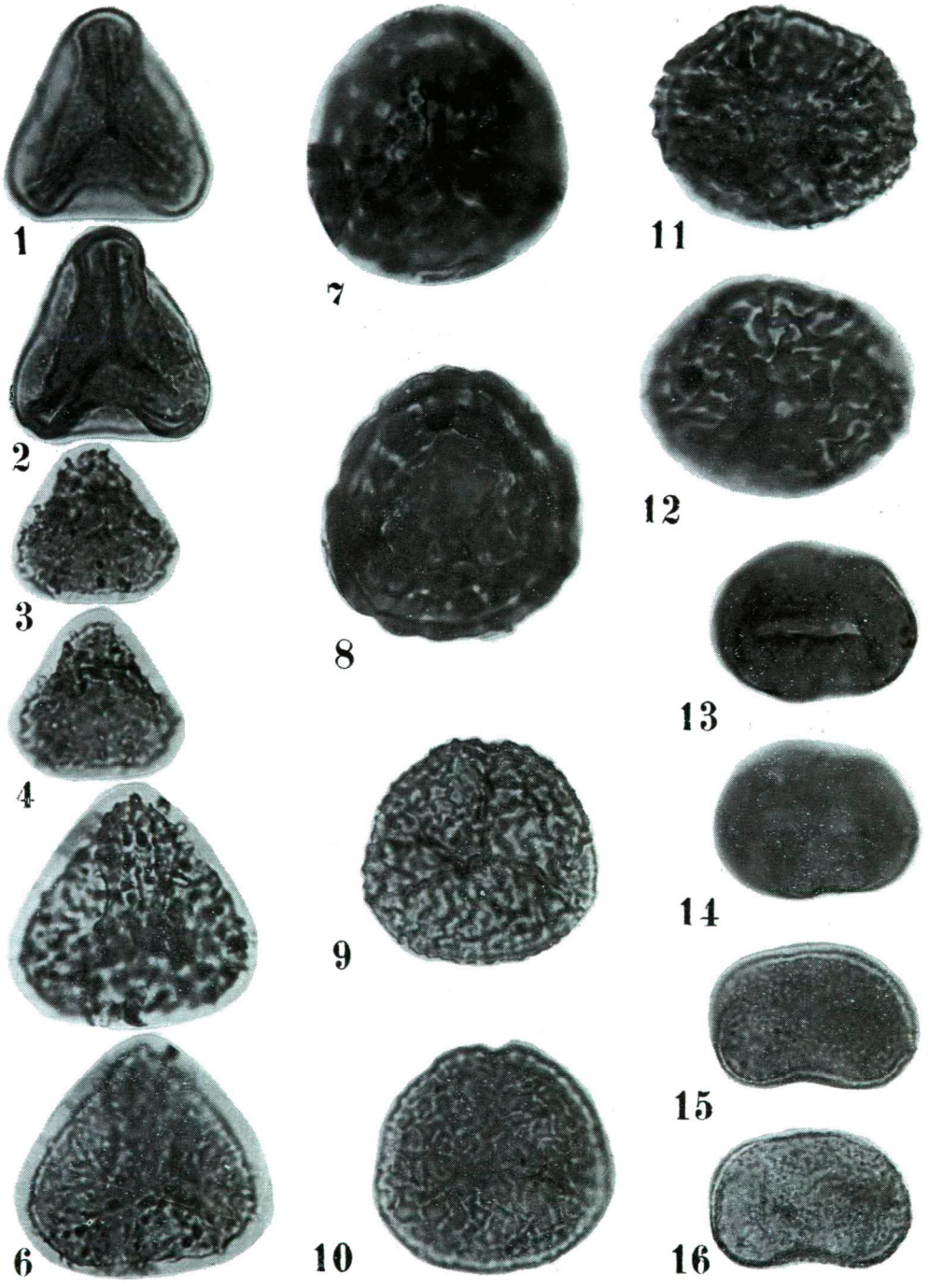


Fig. 1. Toroisporis (Toripunctisporis) hungaricus n. fsp.
o = optical cut, p = proximal surface, d = distal surface

1, 2 — *Toroisporis (Toripunctisporis) hungaricus* n. fsp., holotype.
3, 4 — *Conbaculatisporites* fsp. A.
5, 6 — *Conbaculatisporites* fsp. B.
7, 8 — *Taurocusporites* fsp.
9, 10 — *Camarozonaosporites (Hamulatisporis)* fsp. A.
11, 12 — *Camarozonosporites (Hamulatisporis)* fsp. B.
13, 14 — *Laevigatosporites* cf. *ovatus* WILS. et WEBST. 1946.
15, 16 — *Marattisporites scabratus* COUPER, 1958.
×1000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Diagnosis

From polar visual angle, the contour is triangular with mildly concave side lines. The proximal surface is granular, with grains of about 3 μ wide bases and ending in fine small points and being 1 μ high. The torus is 7 μ wide at the middle line, 4 wide at about the middle of laesures, and widens out at he corners. The ornamentation of torus is identical with that of the proximal surface. The laesures are long, reach the equator and are of finely wavy course. Along the laesures, the thickness of wall is expressed by the form of the collateral line. On the distal side, the ornamental elements are rather flat and of more blurred pattern than on the proximal side. The surface is stained by the thicker and thinner wall parts.

The maximum size is: 30 μ.

Holotype: Table I, 1, 2, prep. U-316—II—9—1/3, No. of cross table: 38,0—103,4.

Locus typicus: Úrkút, Jurassic.

Stratum typicum: Light carbonate manganese ore.

Derivatio nominis: By its occurrence in Hungary.

Differential diagnosis: It is separated from the form species described by KRUTZSCH [1959] first of all by its smaller size.

Fgen.: *Concavisporites* PF. 1953

Subfgen.: *Concavisporites (Concavisporites)*

1. *C. (Concavisporites) polygonalis* KDS. et SICS. 1964 a
2. *C. (Concavisporites) mortoni* [DE JERSEY 1959] DE JERSEY 1962

Subfgen.: *Concavisporites (Obtusisporis* W. KR. 1959)

1. *C. (Obtusisiporis) undulus* KDS. et SICS. 1964 a
2. *C. (Obtusisporis) hexagonalis* KDS. et SICS. 1964 a

Fgen.: *Verrucosisporites* IBRAHIM 1933

1. *V.* cf. *rarus* KDS. et SICS. 1964 a

Fgen.: *Baculatisporites* TH. et PF. 1953

1. *B. spinifer* [THIERG. 1949] KDS. et SICS. 1964 a

Fgen.: *Conbaculatisporites* KLAUS 1960

1. *C.* fsp. A (Table I, 3,4)
2. *C.* fsp. B (Table, I, 5,6)

Fgen.: *Trilites* COOKSON 1947 ex COUPER 1953

1. *T.* cf. *pulcher* KDS. et SICS. 1964 a
2. *T. couperi* KDS. et SICS. 1964 a

Fgen.: *Clavatisporites* KDS. et SICS. 1964 a

1. *Cl. clarus* KDS. et SICS. 1964 a
2. *Cl. pulcher* KDS. et SICS. 1964 a
3. *Cl.* fsp.

Fgen.: *Dictyotriletes* [NAUMOVA 1937] R. POT. et KR. 1954

Subfgen.: *Dictyotriletes* (*Kluisporites* COUPER 1958) POCOCK 1962

1. *D. (Klukisporites) deaki* KDS. et SICS. 1964 a
2. *D. (Klukisporites) variegatus* [COUPER 1958] KDS. et SICS. 1964 a

Fgen.: *Taurocusporites* STOVER 1962

1. Cf. *T.* fsp. (Table I, 7,8)

Fgen.: *Camarozonosporites* PANT 1954 ex R. POT. 1956

Subfgen.: *Camarozonosporites* (*Hamulatisporis* W. KR. 1959)

1. *C. (Hamulatisporis)* fsp. A (Table I, 9, 10)
2. *C. (Hamulatisporis)* fsp. B (Table I, 11, 12)

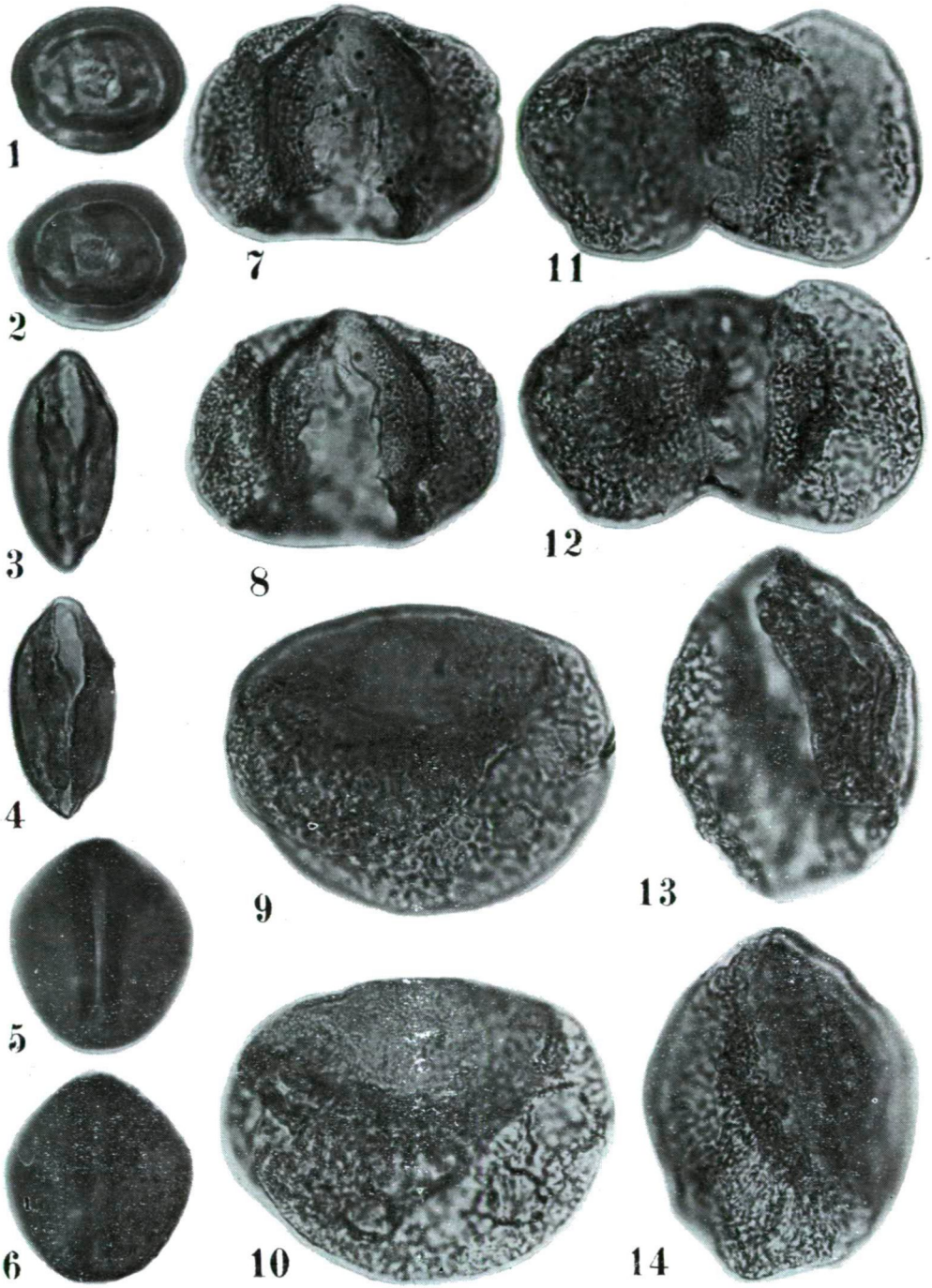
Fgen.: *Laevigatosporites* IBRAHIM 1933

1. *L.* cf. *ovatus* WILS. et WEBST. 1946 (Table I, 13, 14)
Fgen.: *Marattisporites* COUPER 1958
1. *M. scabratus* COUPER 1958 (Table I, 15, 16)
Fgen.: *Spheripollenites* COUPER 1958
1. *S. scabratus* COUPER 1958
2. *S. subgranulatus* COUPER 1958
Fgen.: *Classopollis* [PFLUG 1953] POCOCK et JANS. 1961
1. *C. classoides* [PF. 1953] POCOCK et JANS. 1961
2. *C. minor* POCOCK et JANS. 1961
3. *C. grandis* SICS. et KDS. 1969
Fgen.: *Corollina* [MALYAVKINA 1949] VENK. et GÓCZÁN 1964
1. *C. meyeriana* [KLAUS 1960] VENK. et GÓCZÁN 1964
Fgen.: *Bennettitaceaeacuminella* MALYAVKINA 1953
1. *B.* cf. *simplex* MALYAVKINA 1953
Fgen.: *Ginkgoretectina* MALYAVKINA 1953
1. *G. punctata* MALYAVKINA 1953 (Table II, 3, 4)
2. *G. ferrei* POCOCK 1970 (Table II, 5, 6)
3. *G. fsp.*
Fgen.: *Monosulcites* ERDTMAN 1947, COOKSON 1947 ex COUPER 1953
1. *M. minimus* COOKSON 1947
2. *M. urkutiensis* [SICS. et KDS. 1961] SICS. et KDS. 1969 subfsp. *urkutiensis*
Fgen.: *Eucommiidites* ERDTMAN 1948
1. *E. troedssonii* ERDTMAN 1948 ex COUPER 1958
2. *E. rugulatus* SICS. et KDS. 1969
Fgen.: *Alisporites* DAUGHERTY 1941
1. *A. similis* [BALME 1957] DETTMANN 1963 (Table II, 7, 8)
2. *A. thomasii* [COUPER 1958] POCOCK 1962 (Table II, 9, 10)
3. *A.* fsp. (Table II, 11, 12)
Fgen.: *Parvisaccites* COUPER 1958
1. Cf. *P. enigmatus* COUPER 1958 (Table II, 13, 14)
Fgen.: *Platysaccus* NAUMOVA 1937 ex R. POT. et KLAUS 1954
1. *P.* fsp. (Table III, 1, 2)
Fgen.: *Vitreisporites* LESCHIK 1955
1. *V. pallidus* [REISSINGER, 1938] NILSSON, 1958
2. *V.* cf. *cragii* POCOCK 1970 (Table III, 3, 4)
Fgen.: *Cerebropollenites* NILSSON 1958
1. *C. macroverrucosus* [THIERG. 1949] POCOCK 1970 (Table III, 5, 6).

Apart from sporomorphs, we have found the following more important microfossils: *Tytthodiscus* fsp., *Crassosphaera concinna* COOKSON et MANUM 1960, *Crassosphaera* sp., *Hystrichosphaeridae* div. gen. et sp., *Foraminiferae;* chitin-skeletal remains (Table III, 7, 10).

B) Quantitative results (Fig. 2)

On the basis of the percentage distribution of the spore-pollen data of boring profile there may be separated locally two main layers. From 106.2 until 161.6 m the *Spheripollenites* pollen grains are dominant and besides them, there occur also *Monosulcites minimus* in a considerable percentage. Below them, till 209.3 m, the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quantity of the mentioned pollen grains strongly decreases, the *Classopollis* occurring in a dominant quantity. Inside the two main layers, takint into consideration the finer details, there may be separated from each orther further communities that are important from a facies ecological point of view.

(a) From 209.3 till 204.0 m, that is basis and substratum of the main layer, the composition of sporomorphs is rather mixed. A prominent dominance cannot be observed at either of the groups separated. The high *Pteridophytic* percentage is referring to that a profile part close to the fernery of the vegetation lining the sunk basin. The quantity of pollen grains referring to *Cycadaceae* is high, as well. That is verifying the *Pteridophytic, Cycadaceae* zone, ascertained earlier [KEDVES and SIMONCSICS 1964 a]. Apart from the mentioned sporomorphs, also pollen types *Eucommiidites* are considerable components of the spore-pollen communities. That is referring to that the *Gymnospermatophyte* producing these pollen grains took part in the riverside vegetation, too. In this way, the gymnospermous zone *(Cycadinae — Cheirolepis-Brachyphyllum-Pagiophyllum)* that follows the *Pteridophyte* community is richer than it is in the profile of shaft III in Úrkút. *Crassosphaeridae* occur in a considerable quantity only in that part.

(b) From 204.0 till 178.0 m, in the lower part of the proper main layer, the typical *Classopollis* dominance is representing the zone lying farther from the bank. The fern-spores, beginning from the lower samples of this part, are decreasing with minor fluctuations. In addition to *Spheripollenites,* also the increasing amount of *Monosulcites minimus* is to be mentioned. *Monosulcites urkutiensis* appeared only on the bottom and on top of the region.

(c) Till 161.5 m a gymnospermous zone of transitory character can be established, by a decreasing *Classopollis* quantity that of *Spheripollenites* increases. In the transitional part, also the amount of *Monosulcites urkutiensis* increases somewhat. That is the upper part of the main layer.

(d) From 160.0 till 110.7 m there is a *Spheripollenites* dominance that corresponds to the radiolarian clay marl, accompanied by a considerable, about 20 per cent, amount of *Monosulcites minimus.*

(e) In the upper part of the profile, in the carbonate manganese ore above the main layer (samples 1—3), the sporomorphic composition again changes, referring again to a riverside vegetation, however not of a size like that on the bottom of the profile. The quantity of *Monosulcites minimus* referring to *Cycadaceae* is high or dominant or it is identical with *Spheripollenites.* The quantity of fern-spores has augmented a little, as well.

The organisms indicating the ecology of salt- or brackwater are represented in every sample of the profile at least by one of the three groups *(Hystrichosphaeridae, Crassosphaeridae, Foraminiferae),* they are, however, quantitatively not considerable

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1, 2 — *Corollina meyeriana* [KLAUS 1960] VENK. et GÓCZÁN 1964.
3, 4 — *Ginkgoretectina punctata* MALYAVKINA 1953.
5, 6 — *Ginkgoretectina ferrei* POCOCK 1970.
7, 8 — *Alisporites similis* [BALME 1957] DETTMANN 1963.
9, 10 — *Alisporites thomasii* [COUPER 1958] POCOCK 1962.
11, 12 — *Alisporites* fsp.
13, 14 — *Parvisaccites* cf. *enigmatus* COUPER 1958.
×1000

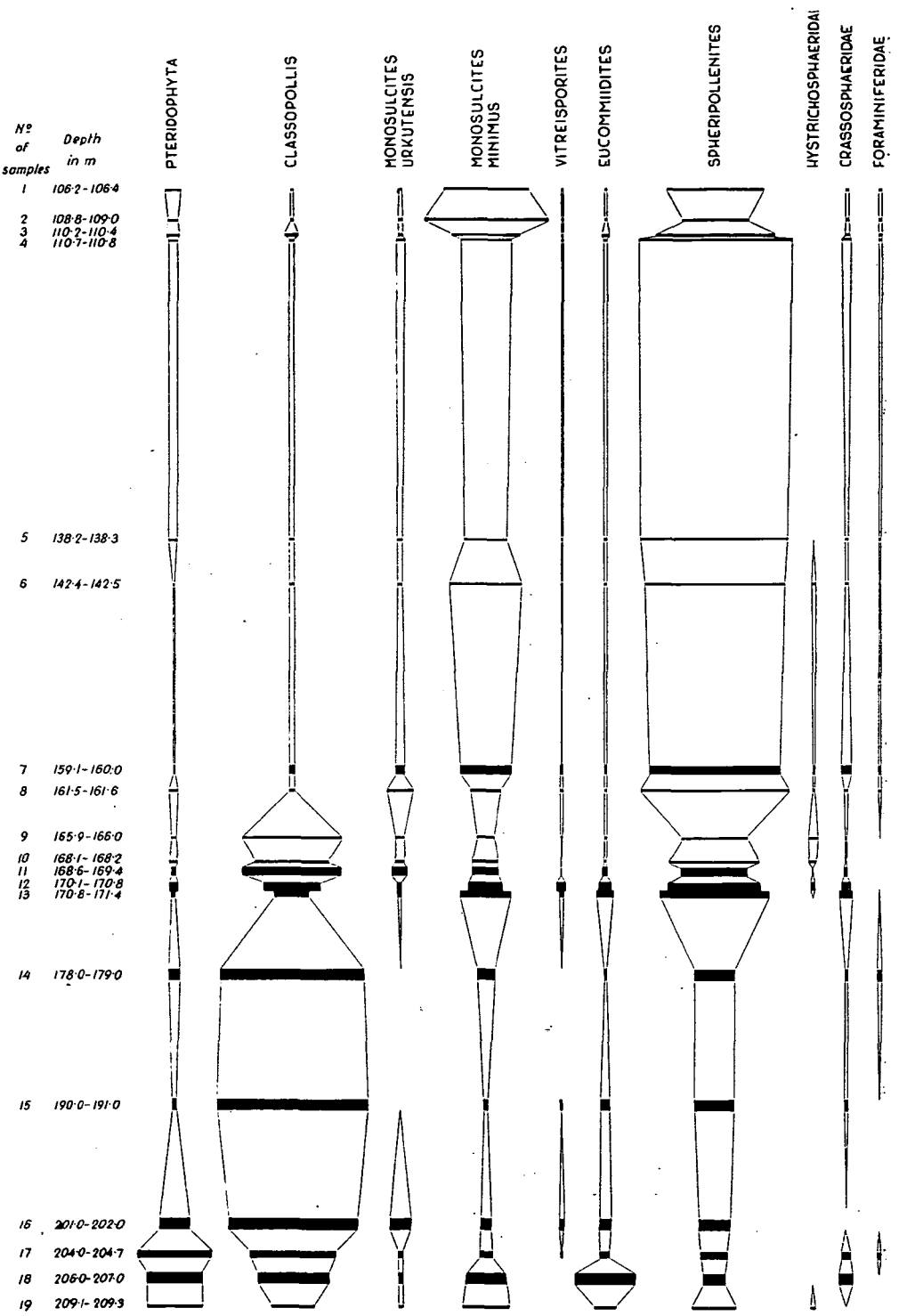


Fig. 2. Contracted diagram of the sporomorphs of the profile investigated

and cannot be factors of the synthesis. The approximately consequent although rare occurrence of the remains of *Foraminiferae* with chitin skeleton is referring to sediments of salt-water (half-salt-water) character along the whole profile.

DISCUSSION OF RESULTS

(1) A large part of the sporomorphs, earlier demonstrated or described in the course of microscope investigations have again occurred in our samples. From among the present matter of investigation only *Toroisporis (Toripunctisporis) hungaricus* n. fsp. has been described. Also the number of spore-pollen types that are new as compared to the above mentioned ones but already published in another place is not low (17). From among the pollen types the pneumatic forms are more frequent than in case of earlier investigations, and the chitin skeletal *Foraminiferae* remains take part first in the present work in the manganese ore at Urkut.

(2) Our earlier statements about the zonation of the vegetation bordering the basin for sediment collection [KEDVES et SIMONCSICS 1964 a] are essentially supported by newer data. In respect of the finer details, on the basis of the layer the larger participation of Coniferae producing the pollen types *Eucommiidites* in the community is worth mentioning. The smaller quantity of plankton organisms may have been also a result of the sporadical defectiveness of sampling or of the fact that every sample was rich in spores and pollen grains. For instance, *Crassosphaeridae* always occurred but in comparatively low quantity, as a separate layer it could not be demonstrated.

(3) Although the lighter and darker parts of several striped samples were separately explored and investigated, we could not establish an essential difference in the spore-pollen composition. We had, therefore, to reject our supposition that the strips may have depended upon the change of seasons.

SUMMARY

We have carried out spore-pollen investigations on sample 20 of the carbonate manganese ore layer group of boring No. 316 at Úrkút. In the course of the investigations we have demonstrated 61 kinds of sporomorphs. From among these one form species is completely new, and seventeen species are new only for the manganese ore in Urkut. Opposite to the aerlier finds, the occurrence of the *Foraminiferae* remains with chitin skeletons in new. Based on quantitative data, there can be separated two main palynologic layers and — in respect of finer details — further facies. The lighter and darker strips of the manganese ore-separated according to the degree of oxidation of the manganese ore — cannot be separated in respect of their spore-pollen material.

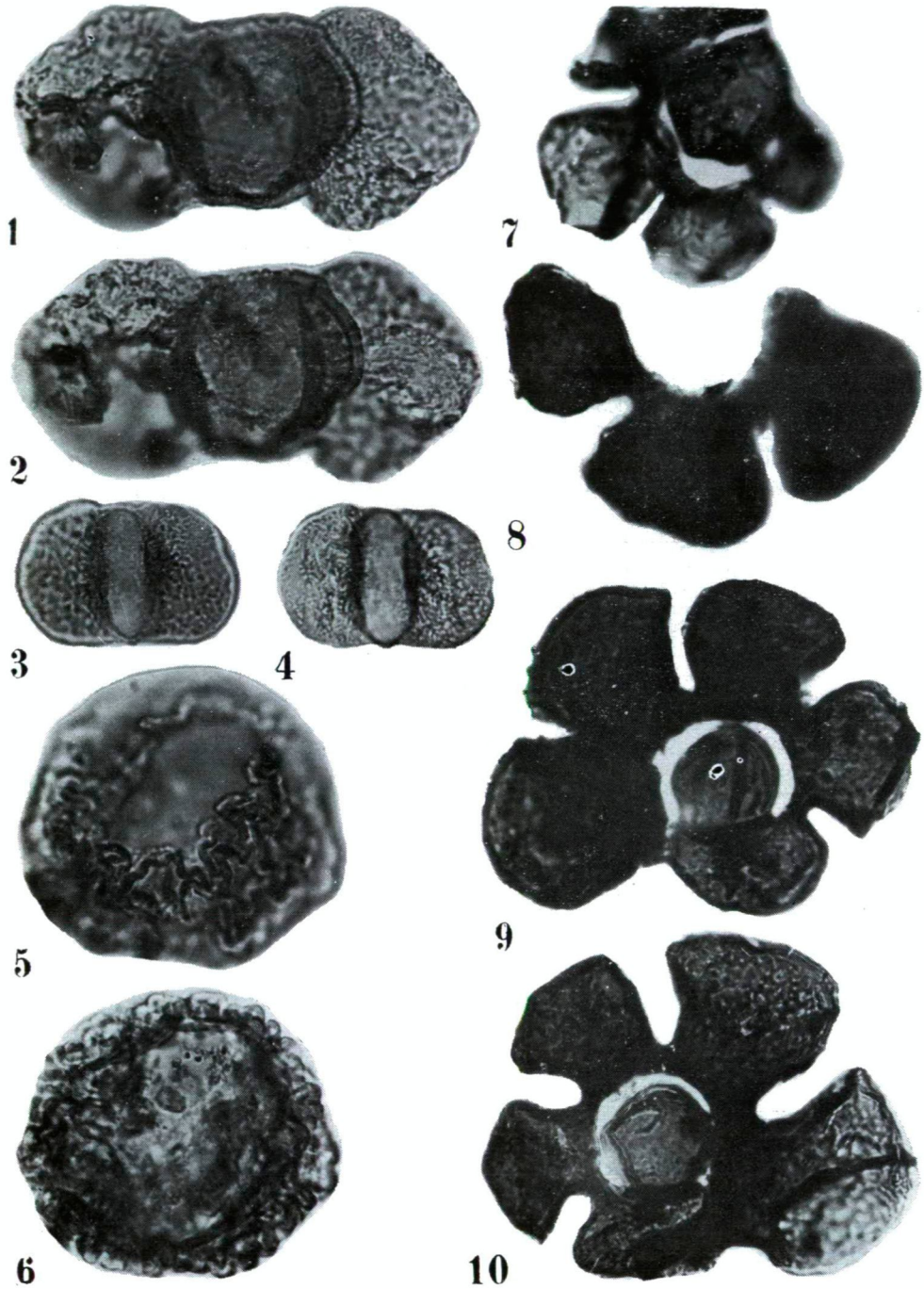
REFERENCES

BALME, G. E. [1957]: Spores and Pollen Grains from the Mesozoic of Western Australia. — C. S. I. R. O. Coal. Res. Ref. T. C., **25**, 1—48.

COOKSON, I. C. [1947]: Plant microfossils from the lignites of the Kerguelen Archipelago. Rep. B. A. N. Z. Antarctic Res. Exped., **A2**, 129—142.

COOKSON, I. C. and MANUM, S. [1960]: On Crassosphaera, a New Genus of Microfossils from Mesozoic and Tertiary Deposits. — Nytt Magasin for Botanik **8**, 5—8.

COUPER, R. A. [1953]: Upper Mesozoic and Cainozoic Spores and Pollen Grains from New Zealand. — Palaeont. Bull. Wellington **22**, 1—77.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COUPER, R. A. [1958]: British Mesozoic Microspores and Pollen Grains. — Palaeontographica **B103,** 75—179.
DAUGHERTY, L. H. [1941]: The Upper Triassic flora of Arizona. — Publs. Carnegie Instn., **526,** 1—108.
DETTMANN, M. E. [1963]: Upper Mesozoic microfloras from South Eastern Australia. — Proc. R. Soc. Vict., **77,** 1—173.
ERDTMAN, G. [1947]: Suggestion for the classification of fossil and recent pollen grains and spores. — Svensk. Bot. T., **41,** 104—114.
ERDTMAN, G. [1948]: Did dicotyledonous plants exist in Jurassic time? — Geol. Forh. Stockholm **70,** 265—271.
IBRAHIM, A. C. [1933]: Sporenformen des Aegirhorizontes des Ruhrreviers. — Diss. TH Berlin, Würzburg (K. Triltsch), 1—47.
JERSEY, N. J. DE [1959]: Jurassic Spores and Pollen Grains from the Rosewood Coalfield. — Mining J., Queensland **60,** 346—366.
KEDVES, M. and SIMONCSICS, P. [1964]: Microstratigraphy of the Carbonate Manganese Ore Layers of the Shaft III of Úrkút on the Basis of Palynological Investigations. — Acta Miner.-Petr. Szeged **16,** 3—48.
KEDVES, M. and SIMONCSICS, P. [1964 b]: Spores nouvelles extraites de minerai de manganèse jurassique de la région d'Úrkút (Hongrie). — Pollen et Spores 6, 605—610.
KLAUS, W. [1960]: Sporen der karnischen Stufe der ostalpinen Trias. — Jb. Geol. B. A **5,** 107—183.
KRUTZSCH, W. [1959]: Mikropaläontologische (sporenpaläontologische) Untersuchungen in der Braunkohle des Geiseltales. — Geologie **8,** BH 21—22, 1—425.
LESCHIK, G. [1955]: Die Keuperflora von Neuewelt bei Basel, II. Iso- und Mikrosporen. — Schweiz. palaeont. Anh., **72,** 9—10.
MALYAVKINA, V. S. [1953]: Spores and Pollen Grains from the Upper Triassic and the lower and Middle Jurassic and the eastern and western parts of the Ural district — (in Russian). — Paleobot. Sbornik, n. s. **75,** 94—159.
NAUMOVA, S. N. [1937]: Spores and Pollen of the coals of the USSR. XVIII. Int. Geol. Congr., Abstract Papers USSR, 1937. Chief Editional Office of the mining-fuel and Geological Prospecting Literature, pp. 60—61, Moscow and Leningrad 1939.
NILSSON, T. [1958]: Über das Vorkommen eines mesozoischen Sapropelgesteins in Schönen. — Lunds. Univ. Arss. n. s. **54,** 1—111.
PANT, D. D. [1954]: Suggestions for the classifications of fossil Spores and Pollen Grains. — Bot. Rev., **20,** 33—60.
POCOCK, S. A. J. [1962]: Microfossil analysis and age determination of strata at the Jurassic-Cretaceous boundary in the western Canada plains. — Palaeontographica **B 111,** 1—95.
POCOCK, S. A. J. [1970]: Palynology of the Jurassic Sediments of Western Canada. — Palaeontographica **B130,** 12—136.
POCOCK, S. A. J. and JANSONIUS, J. [1961]: The pollen genus Classopollis Pflug, 1953. — Micropaleontology **7,** 439—449.
POTONIÉ, R. [1956]: Synopsis der Gattungen der Sporae dispersae I. Sporites. — Beih. Geol. Jb., **23,** 1—103.
POTONIÉ, R. and KREMP, G. [1954]: Die Gattungen der palaeozoischen Sporae dispersae und ihre Stratigraphie. — Geol. Jb., **69,** 111—194.
RAATZ, G. V. [1937]: Mikrobotanisch-stratigraphische Untersuchung der Braunkohle pes Muskauer Bogens. — Abh. preuss. geol. L.-A., n. s., **183,** 1—48.
ROSS, N. E. [1949]: On a Cretaceous pollen and spore bearing clay at Scania. — Bull. Geol. Inst. Upsala **34,** 25—43.
SIMONCSICS, P. and KEDVES, M. [1961]: Paleobotanical Examinations on Manganese Series in Úrkút (Hungary, Transdanubia). — Acta Miner.-Petr. Szeged **14,** 27—57.
SIMONCSICS, P. and KEDVES, M. [1969]: The Pollen Grains of the Carbonate Manganese Ore of the Shaft III in Úrkút. — Acta Miner.-Petr. Szeged **19,** 85—94.

1, 2 — *Platysaccus* fsp.
3, 4 — *Vitreisporites* cf. *cragii* POCOCK 1970.
5, 6 — *Cerebropollenites macroverrucosus* [THIERG. 1949] POCOCK 1970. ×1000.
7, 10 — *Foraminiferae.* ×500.

STOVER, L. E. [1962]: Taurocusporites, a new trilete spore genus from the Lower Cretaceous of Maryland. — Micropaleontology 8, 55—59.
THIERGART, FR. [1949]: Der stratigraphische Wert mesozoischer Pollen und Sporen. — Palaeontographica **B 89**, 1—34.
THOMSON, P. W. and PFLUG, H. D. [1953]: Pollen und Sporen des mitteleuropäischen Tertiärs. — Palaeontographica **B 94**, 1—138.
VENKATACHALA, B. S. and GÓCZÁN, F. [1964]: The spore-pollen flora of the Hungarian „Kössen-Facies". — Acta Geol., Acad. Sci. Hung. **8**, 203—228.

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INVESTIGATION OF MONTMORILLONITES TREATED BY UREA

O. LIBOR, L. GRABER AND É. PÉCSI-DONÁTH

I. INVESTIGATION OF MONTMORILLONITES TREATED BY UREA SOLUTIONS

The behaviour of different clay minerals brought into contact with organic substances was studied in the last years by GREENLAND [1964, 1965], LAFFER, etc. The swelling of three-layer silicates of montmorillonite type in watery as well as in organic agents was studied by GORODNOV [1966], KERNS [1966], MANUILOVA [1966], HAZART [1965], HILTNER [1967], TAYLOR [1965], etc.

Several authors dealt with the interaction of different organic compounds and montmorillonites regarding the swelling of the clay mineral's lattice and the building in of the organic molecules into the lattice. WEISS [1961] dealt with kaolinite-urea, WADA [1959] studied the urea-montmorillonite systems, while SHIGA [1961] investigated the complexes of different cation-montmorillonites formed with urea and their derivatives. MORTLAND [1966] studied the structure of urea-montmorillonite complexes on the basis of their infrared absorption spectra.

Our primary aim was to produce *slowly acting* nitrogeneous chemical fertilizer *which are produced by utilizing clay minerals.* The use of clay mineral was chosen because it is cheap, occurs in the soil and the intensive, motorized soil cultivation had the claim to *slowly acting chemical fertilizers.*

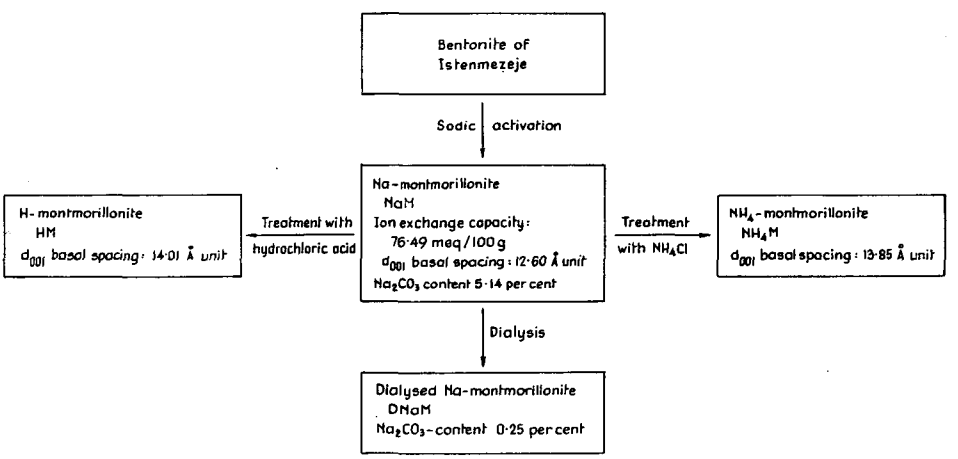

Fig. 1. Origin of the applied samples

Urea is applied on a large-scale for soil and sprinkling fertilizers as fast-acting nitrogen chemical fertilizer. The nitrogen content of the urea is the highest out of the nitrogen chemical fertilizers. In the course of natural biological fertilization urea falls into the soil. Our investigations were performed with clay minerals brought into contact with urea to determine the interaction of the clay minerals of three-layer structure and of the urea brought into contact with them. Na-montmorillonite *(NaM)* from the Istenmezeje bentonite was the starting material and from this sample H-, occasionally NH_4 -clay minerals were prepared *(Fig. 1.)*.

With this cation-montmorillonite experiments were performed in test-tubes. 50 cg samples of air-dry montmorillonite were weighed and 20 ml urea solution of different concentration was added to each sample. The suspensions thus obtained were then held constantly at 30° C. After the certain observations the suspensions were shaken and let rest undisturbed till the next observation.

The concentration of the solutions being in contact with clay minerals was measured from time to time during several months, and the measure of gel-stage and rheological changes of the clay mineral were also registered. The degree of swelling was measured by the gel-volume while its thixotropic change was observed on the basis of its rheological behaviour in the course of tilting of the test-tube. The preparation method is discussed in the previous paper [LIBOR and GRABER, 1969].

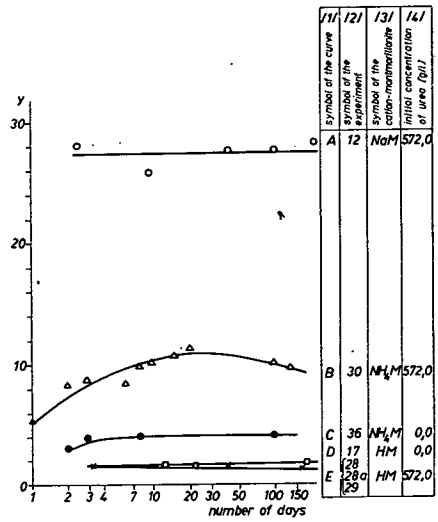

Fig. 2. Swelling of cation montmorillonites y = volume of the swelled gel taking the original volume as 1

Montmorillonites showed better swelling in concentrated urea solution than in distilled water. *NaM* shows the best swelling (it swells at about 28-times of its original volume) and *HM* swells least *(Fig. 2.)*.

In accordance with literature data water plays significant role in swelling of montmorillonites (Table I. a. b.). LIBOR and GRABER [1969] proved that montmorillonites swell hardly or not at all in alcohol.

In distilled water the swelling of *NaM* was unmeasurable because of the total diffusive settlement which was due to the large-scale peptization of the gel.

The *swelling* of montmorillonite caused by the effect of water is influenced by the hydration of the interlayer cations of the lattice, by the surface charge density and by the osmotic feature of the system.

The building in of N-containing compounds into the lattice of montmorillonite depends on the quantity of water in the lattice [SWOBODA and KUNZE, 1965; TAHOUN and MORTLAND, 1966; etc.]. MORTLAND also demonstrated that the proton transfer capacity of the water of air-dry montmorillonites is greater than that of the H_3O^+ ion, depending on the quality of the exchangeable cations of the lattice.

TABLE I

a) Initial composition of experimental solutions I
Aqueous solutions

/1/ Serial number of experiment	/2/ Marking of cation montmorillonite	/3/ Initial concentration of urea solution g/l	/4/ M_1	/5/ M_2	
2	NaM	1,86	0,05	39,94	M_1 = urea g/clay mineral g
7	NaM	102,30	4,09	36,95	M_2 = water g/clay mineral g
12	NaM	572,10	22,88	23,11	
14	NaM	0,0	—	40,00	
17	HM	0,0	—	40,00	
23	HM	104,50	4,18	38,90	Admeasurement
27	HM	504,20	20,01	25,11	in experiments
34	NH_4M	0,0	—	40,00	1—57:0,5 g of
35	NH_4M	572,80	22,91	23,09	cation-montmo-
37	DNaM	0,0	—	40,00	rillonite in
38	DNaM	572,60	22,90	23,82	each case.

b) Initial composition of experimental solutions II

42	NH_4M	0,0	—	31,54	
43	NaM	0,0	—	31,52	
44	HM	0,0	—	31,58	In case
45	DNaM	0,0	—	31,54	of samples
46	NH_4M	0,0	—	32,16	N° 42—45, 50—53
47	NaM	0,0	—	32,16	abs. alcohol,
48	HM	0,0	—	32,08	otherwise etanol
49	DNaM	0,0	—	32,18	of 96 per cent
50	NH_4M	49,4	1,58	30,54	were used.
51	NaM	49,4	1,59	30,61	
52	HM	49,4	1,58	30,56	
53	DNaM	49,4	1,58	30,56	
54	NH_4M	90,2	3,00	32,34	
55	NaM	90,2	3,00	32,34	
56	HM	90,2	3,02	32,40	
57	DNaM	90,2	3,02	32,40	

Fig. 3. shows the process of thixotropy of the *NaM*. This process was completed during several days in concentrated urea solutions while it proved to be a long-lasting process in diluted solutions. *HM* did not swell under the experimental conditions thus thixotropy could not be observed.

Dissolving investigations were also performed from the gel swelled in concentrated urea solution to determine whether the montmorillonite swelled in diluted urea solution for a longer time possesses or not urea-retaining feature.

The watery gel was dried (above $CaCl_2$, at room-temperature) and water was dropped on it. The quantity of dissolving urea was determined and the montmorillonite was dried again. This process was repeated several times always drying the sample. Granular and pulverized urea which does not contain clay mineral as well as urea mixed with quartz powder were also investigated.

The urea which did not contain clay mineral totally dissolved practically in two steps. The dissolving of urea from the *HM*-urea took place in about nine steps. The *NaM*-urea contained about 30 per cent of the original urea content after twelve steps (Table. II.).

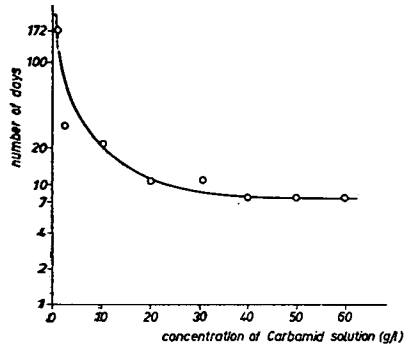

Fig. 3. Thixotropic time of Na-montmorillonite as a function of the concentration of urea

TABLE II

Investigation of urea-retaining capacity of NaM, HM *and* NH_4M

Sign of clay mineral	NaM	HM	NH_4M			
Number of dissolving steps	Dissolved urea in per cent*					
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	12	26	26	60	60	83
2	20	38	24	100	92	98
3	28	64	31		100	99
4	35	81	39			
5	41	89	49			
6	47	93	61			
7	52	94	71			
8	57	95	80			
9	59	97	89			
10	62		95			
11	68					
12	71					

* Concerning the initial quantity of urea.
(5) Urea was previously mixed with quartz powder, the quantity of which corresponded to that of the clay mineral content.
(6) Granular urea without clay minerals.
(7) Pulverized urea without clay minerals.

X-ray diffractometric base reflexion measurements were also done to determine the entering and binding forms of urea into the montmorillonite lattice. These measurements were done by GY. BÁRDOSSY*, with pulverized gels dried above $CaCl_2$ (Table. III., *Fig. 4.*)

TABLE III

Change of the basal plane distance (d_{001}) of montmorillonites swelled in aqueous urea solutions

Sign of cation — montmorillonite	Original d_{001} Å	d_{001} Å swelled in aqueous urea solutions	Change of d_{001} Å
NaM	12,95	18,22	5,63
HM	14,04	13,51	—0,53

The elementar cell of the urea crystal is built up by two urea molecules *(Fig. 5.)*. The "*a*" and "*b*" coordinates of the elementar cell are both 5.67 Å unit. While the base reflexion of the air-dry *NaM* swelled in diluted urea solution increased by 5.62 Å unit, it is presumable that the urea crystal layer, consisting of one elementar cell, lies between the basal spaces of the montmorillonite, the "*c*" axis of which is perpendicular to that of the montmorillonite lattice. In *HM* the d_{001} base reflexion decreased by 0,53 Å unit, urea did not enter the lattice.

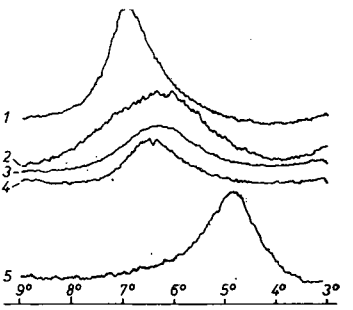

Fig. 4. X-ray-diffraction diagram of cation-montmorillonites *1.* Original Na-montmorillonite, d_{001} spacing = 12.60 Å *2.* Original NH_4-montmorillonite, d_{001} spacing = 13.86 Å *3.* Original H-montmorillonite, d_{001} spacing = 14,04 Å *4.* Experiment No. 23. H-montmorillonite, previously swelled in 10 % urea solution d_{001}, spacing = 13,51 Å. *5.* Experiment No. *7.* Na-montmorillonite, previously swelled in 10 % urea solution, d_{001} spacing = 18,22 Å. Basis reflection is calculated according to the peak of basal spacing.

From these investigations it is obvious that the two cation-montmorillonites are of different behaviour. The influencing role of cations was emphasized by EMERSON [1963] and SHIGA [1961]. According to them the greater the charge of the exchangeable cations of the montmorillonite, it can bind the more organic molecules. The role

* Senior scientist of the Geochemical Research Laboratory of the Hungarian Academy of Sciences.

of the exchangeable cations of the montmorillonite lattice, in connection with the swelling and urea-binding capacity of the lattice is probably influenced by its hydration capacity [NORRISH, 1954]. The relative charge density of the cations is the following:

$$Al^{3+} > Fe^{3+} > Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^{+} > K^{+} > H^{+} > NH_4^{+}$$

From these data it is obvious that the charge density of the K^+, H^+ and NH_4^+ ions is the least and are about of same value. The charge density considerably influences the measure of the ions' hydration. The hydration energy, resp. the number of stronger bound water molecules of the ions of small relative charge density are least.

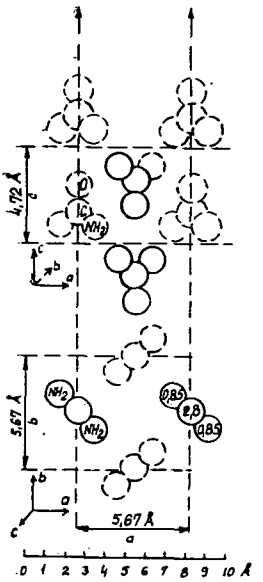

Fig. 5. Projection of urea.

The smaller size swelling and urea-binding capacity of the *HM* and NH_4M observed both by SHIGA [1961] and authors are possibly in connection with the smaller hydration ability which is connected to the charge density of low value of the H^+ and NH_4^+ ions.

The interaction of *HM* and *NaM* with the urea in watery agent is different and the dissimilarity between their cations is responsible for this difference. Urea penetrates the basal spaces of the lattice of *NaM*, and it does not that in case of *HM*.

To prove these facts derivatographic investigations were also performed. The prepared different cation-montmorillonites treated by urea as mentioned above were heated by a heating gradient of 10° C/min. To explain the thermal behaviour of the urea-containing clay minerals the derivatograms of the *HM* and *NaM* were also completed at the same temperature gradients *(Figs. 6, 7)*. It was necessary to investigate the urea itself under the same conditions to explain the thermal behaviour of the montmorillonite-urea system.

II. THERMAL INVESTIGATION OF THE UREA

The chemical reactions taking place in the course of the thermal transformation of the urea pass off simultaneously in the certain thermal intervals. These reactions are influenced by the heating velocity of the reaction mixture and by the time spent on the temperature in question [KERNS, 1966; MORTLAND, 1968; etc.].

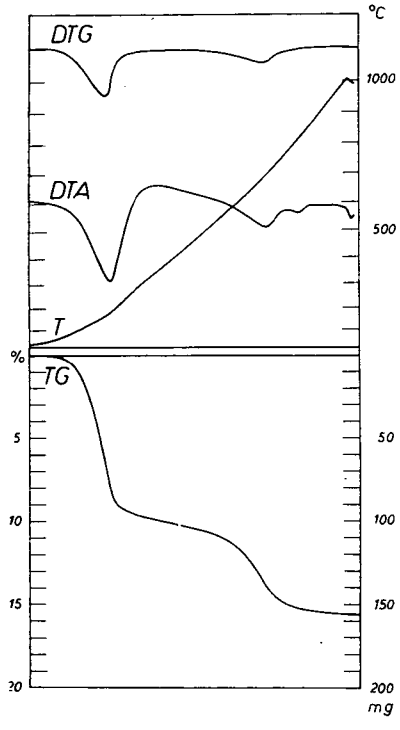

Fig. 6. Derivatogram of H-montmorillonite. Sample: 320 mg. T 1200 DTA 1/5, DTG 1/10, TG 50 mg.

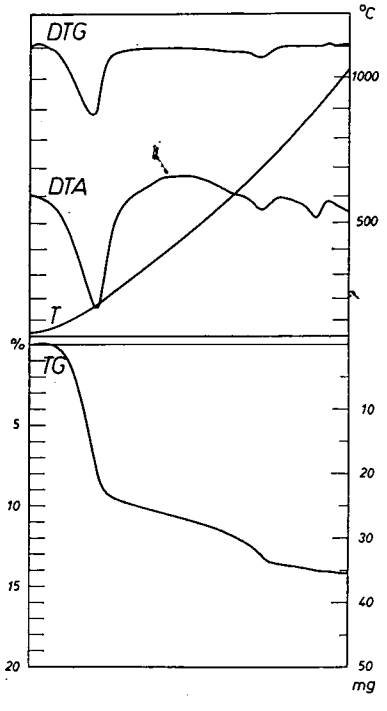

Fig. 7. Derivatogram of Na-montmorillonite. Sample: 1000 mg. T 1200, DTA 1/15, DTG 1/15, TG 200 mg.

Our derivatogram of urea was evaluated on the basis of the data of literature and we tried to explain the reactions which may be connected to the certain peaks of the DTA curve. As a result after melting the urea decomposes to cyanic acid and ammonia. The developing cyanic acid transforms with the urea to in statu nascendi biuret. Above 190 °C this melts and in the interval between 190 and 240 °C cyanic acid and ammonia forms from the biuret [SCHILTKNECHT 1963]. This transformation is connected to a loss of weight of 20 per cent. According to several authors above 190 °C biuret decomposes to urea and cyanic acid and the effect of further heating causes the formation of cyanuric acid and amelide [GIGER, 1958]. At 225 °C besides these reactions cyanuric acid and ammonia develops from the urea [KINOSHITA, 1954; MALKINA and KASARNOVSKI, 1961].

Strong endothermal change can be observed between 220 and 240 °C which is connected to large loss of weight (about 10.5 per cent). At temperatures between

240 and 260 °C a loss of weight of 14.7 per cent results. Then the biuret transforms with cyanic acid into cyanuric acid and cyanic acid is trimerizated to cyanuric acid [MALKINA and KASARNOVSKI, 1957; SCHILTKNECHT, 1963]. Besides these reactions the biuret and cyanic acid have also possibly a reaction during which amelide forms parallel with water loss [WERNER, 1923]. The water formed in such a way reacts with the presenting cyanic acid during which carbon dioxide and ammonia forms [LIENHARD, 1954; SCHILTKNECHT, 1963]. These may cause the observed change of weight. In the course of the thermal decomposition of urea it hardens at 250 °C [SCHILTKNECHT, 1963], which is preceded by strong gas formation. This latter reaction connected to strong gas formation takes place also at this temperature . The thermal gradient curve of the derivatogram remains constant in the course of the reaction and this indicates the strongly endothermal change of it *(Fig. 8.)*.

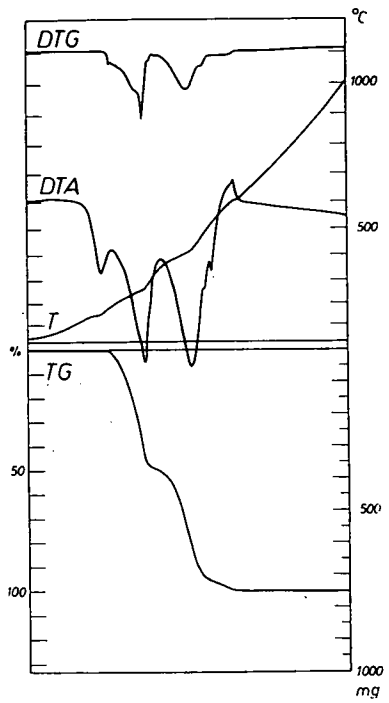

Fig. 8. Derivatogram of urea. Sample: 750 mg. DTA 1/20, DTG 1/15, TG 1000 mg, T 1200° C.

According to SCHILTKNECHT [1963] chain-polymer develops between 240 and 260 °C, which is insoluble in water. Therefore it is possible that there are simultaneous reactions. On the basis of the derivatogram only 4 per cent of loss of weight occurred in the interval of 260 to 280 °C. In this temperature interval possibly polymerization reactions form the main reactions. In the course of these reactions cyanuric acid [MALKINA and KASARNOVSKI, 1961; SCHILTKNECHT, 1963], amelide, ameline, melamine [KINOSHITA, 1954] and melam [FINKELSTEIN and ZAGRANICHNI, 1955] developed. The reaction is connected with exothermal reaction and this relates to the formation of greater quantity of the cyanuric acid [SCHILTKNECHT, 1963]. This exothermal

reaction is shown by the peak of the DTA curve at 300 °C. After melting above 380 °C the polymeric compounds decompose to cyanic acid [FINKELSTEIN and ZAGRANICHNI, 1955; HUNN, 1959; LIENHARD, 1954, SCHILTKNECHT, 1963].

Further five transformations have to be taken into consideration. Out of these changes there are three endothermal (at 420, 480, 520 °C) and two exothermal peak maximums (at 580 and 600 °C). The endothermal peak of 420 °C is in connection with the greatest loss of weight (42 per cent). This may be caused considerably by the leaving of ammonia and carbon dioxide which are the final decomposition products. The explanation of the endothermal processes pertaining to the peaks of 480 and 520 °C and connected to the loss of weight, as well as of the processes pertaining to 500 and 600 °C need further investigations. In literature there are data of the thermal change of urea only up to 500 °C. The loss of weight reaches 100 per cent at 600 °C.*

III. THERMAL INVESTIGATIONS OF MONTMORILLONITES AND THOSE OF UREA CONTENT

The derivatogram of the recorded pure *HM* and *NaM* (*Figs. 6, 7*) agrees well with the data of literature.

In case of the derivatograms of the urea-containing *HM* and *NaM*, however, there are characteristics which have to be explained.

In case of the urea-containing *NaM* (*Fig. 9.* and Table IV.) peak maxima characteristic of urea can be registered at 140, 250, 410 and 540 °C, and the characteristic peak maximums of pure *NaM* also occur at 690 and 820 °C. It is obvious from these facts that the common presence of the two materials has no significant influence on their thermal decomposition.

TABLE IV

Loss of weight of urea-containing Na-*montmorillonite on the basis of its derivatogram*

Temperature and character of peak maximums °C	Loss of weight pertaining to a given temperature °C	per cent	Loss of weight pertaining to the temperature interval °C	per cent
140 endoth.	160	3,45	0—160	3,45
	195	14,42	160—195	10,97
220 endoth.	230	21,14	195—230	6,72
250 endoth.	300	31,43	230—300	10,29
	320	33,71	300—320	2,28
	360	36,57	320—360	2,86
410 endoth.				
450 endoth.	450	46,85	360—450	10,28
540 endoth.	530	51,71	450—530	4,86
	580	53,71	530—580	2,00
690 endoth.			580—740	1,72
820 endoth.	740	55.43		

* The quantitative evaluation of the derivatogram of urea is recently impossible. While reactions, connected to the thermal decomposition of the urea take place simultaneously and in function of the thermal gradient, they are differently evaluated by different authors. Only the presumable explanation of the urea's derivatogram could be given.

The derivatogram of the urea-containing *HM* (*Fig. 10.* and Table V.), however differs considerably from the curves of both the pure urea and the pure *HM*. The peak characteristic of the melting of urea decreased to 115 °C. It is conspicuous that the strong endothermal peak, characteristic of the thermal decomposition of urea at 420 °C, disappeared and instead of it small endothermal peak maximum occurs at

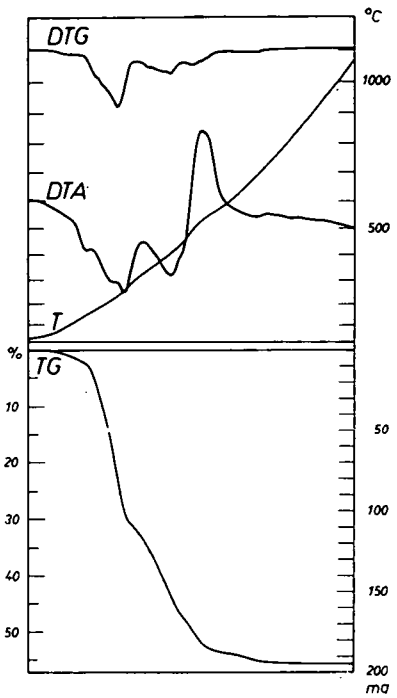

Fig. 9. Derivatogram of urea containing *NaM*. Sample: 350 mg. DTA 1/15, DTG 1/15, TG 200 mg, T 1200° C.

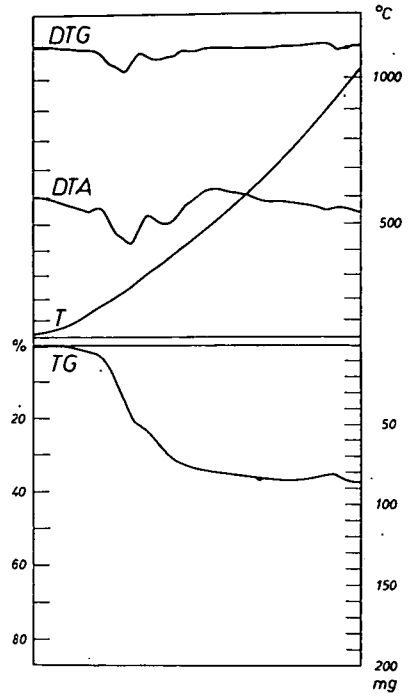

Fig. 10. Derivatogram of urea containing *HM*. Sample: 230 mg. DTA 1/15, DTG 1/15, TG 200 mg, T 1200° C.

360 °C which may presumably derive from different processes. The exothermal peak, characteristic of the urea's thermal decomposition at 520 °C, also disappeared which can be registered in case of urea-containing *NaM*.

The dissimilar behaviour of the *NaM*-, resp., *HM*-urea observed in the course of their thermal decomposition, shows the different urea-bond of the two clay minerals. Both montmorillonites fixed the certain part of urea on their surfaces (endothermal peaks at low temperatures). The endothermal peaks of the two substances at low temperature are dissimilar and this fact shows different urea quantities bound by the two different cation-montmorillonites on their surface.

The *HM* of acidic behaviour [GLAESER, MANTIN, MERING, 1963; POMMER and CARRELL, 1960; SAWHNEY and FRINK, 1966] reacts to urea, showing slightly basic behaviour [SABALITSCHKA and KUBISCH, 1924], presumably according to acid-base reaction. (This is also justified by the structure investigation of MORTLAND, 1966 and HARTER, 1967, done by IR-method.) The formed *HM*-urea molecule-compound

[WERNER, 1923] presumably hinders the entering of water, resp. urea molecules the lattice of the clay mineral. Therefore, in the course of the thermal decomposition of the *HM*-urea the selectivity cannot be observed, the two substances have a mutual influence on their thermal decomposition, and the *HM* brought into contact with diluted urea solution swells only in a small degree [LIBOR and GRABER, 1969].

TABLE V

Data of loss of weight of urea-containing H-montmorillonite on the basis of its derivatogram

Temperature and character of peak maximums °C	Loss of weight pertaining to a given temperature °C per cent	Loss of weight pertaining to the temperature interval °C per cent
130 endoth.	120 1,15	
160 endoth.	160 1,34	0—160 1,34
		160—195 5,18
210 endoth.	220 12,04	220—300 10,56
250 endoth.	300 22,60	
310 endoth.		
360 endoth.	420 23,17	300—420 9,57
440 endoth.		
500 exoth.	495 34,34	420—495 2,17
610 exoth.		
670 endoth.	740 36,52	495—740 2,18
890 endoth.		

TABLE VI

Data on the changes of the weight of urea and clay-minerals containing urea on the basis of the TG curves of the derivatogram and of the material balance

Materials examined	Decrease of weight % of the total urea present			Evaporated moisture, per cent of the initial material
	420—600 °C	300—460 °C	0—300 °C	
Urea	8,0	42,7	49,3	—
H-montmorillonit-urea	9,6	30,2	60,4	3,5
Na-montmorillonit-urea	23,7	53,0	23,3	24,5

The *NaM* bound the urea in two different ways. The urea was partly connected to the surface of the clay mineral's lattice, but dissimilarly to the chemical bond characteristic of the *HM*-urea. On the DTA curve of the derivatogram the peaks characteristic of both the urea and the *NaM* can be separatedly registered. Certain part of urea enters the clay mineral's lattice. This is proved by the fact that the characteristic peaks of both the *NaM* and urea appear (though they mutually influence their thermal decomposition), and the endothermal peak indicating the final decomposition of urea occurs, as well. In the temperature interval of 420 to 600 °C the losses of weight, related to the total urea quantity of the system, are nearly of the same value in case of *HM*-urea, while in case of *NaM*-urea the loss of weight is nearly three times greater than those of the values given below (Table VI; columns

2 and *4*). In case of urea and urea-contanining *HM* the loss of weight observed at ow temperatures (0 to 300 °C) proved to be considerably greater than in case of urea-containing *NaM*. The decompositions of medium temperatures (300 to 420 °C) do not show differences of this measure. These data prove that the H-and *NaM* bind the urea in different ways and that *NaM* binds it in its crystal structure.

As a summary the following facts were stated: the urea molecule enters the lattice of *NaM*; the quality of the exchangeable cations influences this entering; the bond of H-, resp. *NaM* is different; it can be proved by derivatograph that *HM* bound chemically the considerable part of urea on its lattice-surface; the *NaM* partially bound the urea presumably not in chemical way, while the other part of urea was bound in the lattice of the clay mineral [LIBOR, GRABER, DONÁTH, 1970].

TABLE VII

Thermal investigation of Na-, H-, NH_4M-urea melting systems

Number of investigation	Sign of Montmorillonite	Montmorillonite: urea ratio	Heating velocity °C/min.	Length of time of heating min.	Note
Karbamid	—	—	1200/100		
			600/100		
I.			600/150		
			600/100 + 600/400	720	
A 1.	NaM	1:0,35	600/100		
2.	NaM	1:0,35	600/100 + 600/400	90	
B 1.	HM	1:0,35	600/100		Keeping the mixture at 132° C for 4 hours
II.					
2.	HM	1:0,35	600/100 + 600/400	360	
C 1.	NH_4M	1:0,35	1200/100		
A 1.	NaM	1:0,35	300/100		At 130 and 200° C temperature was kept for 15—15 minutes
B 2.	HM	1:0,35	300/100		
III.					
A 1.	NaM	1:0,25	1000/100	100	10 minutes at 130° C and further heating by the given temperature gradient
2.	NaM	1:0,50	1000/100	100	
IV. 3.	NaM	1:0,75	1000/100	100	
4.	NaM	1:1	1000/100	100	
B 1.	NH_4M		1000/100	100	
2.	NH_4M	1:0,30	1200° C/100	100	

On the basis of our investigations the specially formed *NaM* and *HM* seems to be able for utilizing as chemical fertilizer, first of all due to the urea-retaining capacity.

IV. INVESTIGATION OF Na-, H- AND NH_4M — UREA MELTS

1. Heating the pure urea up to its melting point by different thermal gradients and keeping it at this temperature (130 °C) for various length of time, we observed that urea reaching its melting point does not decompose. Keeping the

system at the melting point in different times, slow and continuous thermal decomposition commenced. This decomposition depended on the heating gradient and time, but after 12 hours heating we could not observe the equilibrium (Table VII/I).

2. The following step was to heat the mixtures of Na-, H- and NH_4M — urea of 1:0,35 ratio in the same way and the systems were kept at the melting point of urea for various length of time. Our aim was to investigate that the temporal thermal decomposition of urea is influenced or not by the presence of different cation-containing clay minerals (Table VII/II).

The results demonstrated in every case that, independently of the cation's quality bound to montmorillonite, endothermal reaction resulted parallel with considerable loss of weight. On the one hand the measure of this loss of weight depended on the cation's quality, and was connected to the endothermal reaction, on the other. Further it was also observed that in contrary of the thermal decomposition of pure urea the equilibrium resulted in case of heatings of shorter times. The time of the attainment of equilibrium depended on the cation's quality bound to the montmorillonite. This time proved to be 4 hours in case of *NaM*-urea and 6 hours in case *HM*-urea system. This experience proved that one part of urea enters the *NaM* in such cases too, when urea contacts it as a melt. It is also conspicuous that urea being in contact with the surface of montmorillonite shows more difficult decomposition in case of *HM* than in case of *NaM*-urea system. It is therefore presumable that urea reacts chemically to *HM* also in the melt.

These statements are justified by the experiments in the course of which the mixture of 1:0,35 ratio of the *Na*-and *HM* - urea was heated by 300 °C/100 min. heating velocity and the system was kept at 130 and 200 °C for 15—15 minutes in the course of heating (Table VII/II).

Results show that in the *HM*-urea system, in contrary of the *NaM*-urea system, an endothermal peak occurs at 95 °C which is followed by an exothermal peak at 125 °C (Table VII/III). The further thermal decomposition takes place similarly to that of the *NaM*-urea system. This energetic change may indicate the chemical bond forming between the *HM* and the urea.

The experiments of the fourth group of Table VII/IV were performed to establish the minimal clay mineral/urea ratio, in which case the presence of urea has some influence on the thermal decomposition of the clay mineral. On the basis of the experiments' results this phenomenon occurred at a clay mineral/urea ratio of 1:0.35.

SUMMARY

H-, Na- and *HN_4M* brought into contact with urea were investigated. Investigations included clay minerals brought into contact with urea in solution and melt.

Authors stated that the bound of urea to montmorillonite was dependent on the cation's quality.

1. Two molecule layer of urea was bound in the lattice of *NaM*. After the desiccation of the gel urea crystallized in the lattice of the clay mineral which lies in an elementar celi layer between the d_{001} basal spaces of the *NaM*. The "*c*" axis of urea crystal is perpendicular to that of the montmorillonite lattice.

   The investigated cation-montmorillonites swelled in a slight degree in ethanolic urea solution and this was hardly influenced by the quality of

the exchangeable cations. These data also prove the significance of water in the swelling of montmorillonite.

2. Regarding the thermal behaviour of *H*-, and *NaM* brought into contact with diluted urea solution the fact could be also stated that the urea-bond of the two cation-montmorillonites is different.

   HM bound chemically the considerable part of urea on the surface its lattice. *NaM* bound the one part of urea on its surface presumably not by chemical bond, the other part of urea was bound in the lattice of the clay mineral. This statement agrees with the results of the preliminary performed X-ray diffractometric investigations.

3. The *H*-, *Na*- and NH_4M being in contact with urea melt showed dissimilar thermal behaviour. These results also showed that urea in solution may bind to these montmorillonites in the same way as in watery agent.

REFERENCES

EMERSON, W. W. [1963]: The Effect of Polymers on the Swelling of Montmorillonite. J. Soil Sci. **14**, 52—63.

Финкельштейн, А. И., Заграничный, В. И. [1955]: Спектры поглощения производных триазина в ультрафиолетовой области. Журнал физической химии, XXIX, II, 1937-1941.

GIGER, P. [1958]: Zum Reactionsmechanismus der Bildung von Melamin aus Harnstoff. Promotionsarbeit Nr. *2755*, E. T. H. Zürich.

GLAESER, R., MANTIN, I., MERING, J. [1961]: The Acidity of Montmorillonite. Intern. Geol. Congr. Rept. 21st, Copenhagen *1960*. Pt. 24, 28—34. cit. C. A. **58**, 360b (1963).

Городнов, В. Д., Алель, И. Б. [1966]: Набухвние модифицированных бентонитов. Физика и Гидродинамика нефтяново пласта, 57, 185-188.

GREENLAND, D. J., QUIRK, J. P., THENG, B. K. G. [1964]: Influence of Increasing Proportions of Exchangeable Alkylammonium Ions on the Swelling of Calcium Montmorillonite in Water. J. Colloid Sci. **19**, 837—840.

GREENLAND, D. J. [1965]: Interaction between Clays and Organic Compounds in Soil II. Adsorption of Soil Organic Compounds and its Effect on Soil Properties. Soil Fertilizers **28**, 521—532.

HARTER, R. D. [1967]: Acidity dependent Reactions between Organic Acids and Amines and Montmorillonitic Clay Surfaces. Diss. Abstr. B. *27*(7), 2226.

HAZART, J. P., WEY. R. [1965]: Etude cinétique du gonflement de la montmorillonite en présence d'éthylène glycol an moyen de la diffraction X. Bull. Serv. Carte Géol. Abs. Lorr. *18*, 191—216.

HILTNER, P. A. [1967]: Swelling of Alkyl-ammonium Montmorillonites. Diss. Abstr. B. *28*(5), 1881.

HUNN, F. A. [1959]: Über die Pyrolyse von Harnstoff in Gegenwart von ammoniak. Promotionsarbeit Nr. *2838*, E. T. H. Zürich.

KERNS, R. R. JR. [1966]: Structural Charge Site Influence on the Interlayer Properties of Expandable three-layer Clay Minerals. Diss. Abstr. B. *27*, 1230.

KINOSHITA, H. [1954]: Synthesis of Melamine from Urea II. Rev. Phys. Chem. Japan, *24*, 19—27. it. C. A. *49*, 14007, (1955).

KINOSHITA, H. [1954]: Synthesis of Melamine from Urea III. Rev. Phys. Chem. Japan, *24*, 67—73. cit. C. A. *50*, 1041c, (1956).

LAFFER, B. G., POZNER, A. M., QUIRK, J. P. [1966]: Hysteresis in the Crystalline Swelling of Montmorillonite. Clay Miner. *6*, 311—321.

LIBOR, O., K. GRABER, L. [1969]: Karbamiddal érintkező montmorillonitok vizsgálata I. Karbamidoldatokkal érintkezésbe hozott montmorillonitok vizsgálata. (Investigation of Montmorillonites Contacting Urea. I. Investigation of Montmorillonites Contacting Solutions of Urea. (In Hungarian with an English resumé). Agrokémia és Talajtan *18*, 431—452.

LIBOR, O., K. GRABER, L., P. DONÁTH, E. [1970]: Karbamiddal érintkező montmorillonitok vizsgálata II. Karbamidot tartalmazó Na— és H— montmorillonit termikus vizsgálata. (Investigation on Montmorillonites Contacting Urea. II. Thermic Examination of Na— and H— Montmorillonites Containing Urea. (In Hungarian with an English resumé). Agrokémia és Talajtan, *19*, 293—310.

LIENHARD, E. [1954]: Beitrag zur Kenntnis der thermischen Zersetzung von Harnstoff. Promotionsarbeit. Nr. *2344*, E. T. H. Zürich.
MALKINA, N. I., KAZARNOVSZKIJ, SZ. N. [1957]: The Study of the Mechanism of Formation of Products during the Synthesis of Cyanuric Acid from Urea. Trudy Gor'kovsk Politezk. Inst. *13*, 32-6 (1957). C. A. *54*, 1538b (1960).
Малкина, Н. И., Казарновский, С. Н. [1961]: Синтез лиануровой из мочевмны. Журнал прикл.химии, *34*, 1583-1587
Мануилова, Н. С., Суханова. С. М., Варламов, В. П. [1966]; Участие воды в процесса вспрчивания бентонитов. Эксперимент втехнической минералогии и петрографии, Щздательство „Наука", Москва, 69-73.
MORTLAND, M. M. [1968]: Protonation of Compounds at Clay Mineral Surfaces. 9th Intern. Congr. Soil Sci. Bucharest, Transact. *1*, 691—699.
MORTLAND, M. M. [1966]: Urea Complexes with Montmorillonite, an Infrared Adsorption Study. Clay Minerals, *6*, 143—156.
NORRISH, K. [1954]: The Swelling of Montmorillonite. Disc. Faraday Soc. *18*, 120—134.
POMMER, A. M., CARROLL, D. [1960]: Interpretation of Potentiometric Titration of H-montmorillonite. Nature (*185*/4705), 594—596.
SABALITSCHKA, TH., KUBISCH, G. [1924]: Der Einfluß der Base auf den Grad der Umsetzung primärer Salze zweibasischer Säuren in wäßriger Lösung. Z. Anorg. Allg. Chem. *134*, 79—86.
SAWHNEY, B. L., FRINK, C. R. [1966]: Potentiometric Titration of Acid Montmorillonite. Soil Sci. Soc. Amer. Proc. *3*, 181—184.
SCHILTKNECHT, F. J. [1963]: Über den Reactionsmechanismus der Pyrolyse von Harnstoff zu Cyanursäure. Promotionsarbeit Nr. *3403*, E. T. H. Zürich.
SHIGA, Y. [1961]: Studies on the Complexes of Montmorillonites with Urea and its Derivatives I. The Influences of Exchangeable Cations on the Interlayer Adsorption of Urea by Montmorines. Soil Sci. Plant Nutr. 7(3), 119—124.
SWOBODA, A. R., KUNZE, G. W. [1965]: Infrared Study of Pyridine Adsorbed on Montmorillonite Surfaces. Clays and Clay Minerals, 13th Conf. 277—288. Pergamon Press, Oxford.
TAHOUN, S. A., MORTLAND, M. M. [1966]: Complexes of Montmorillonite with primary, secondary, and tertiary Amides: I. Protonation. Soil Sci. *102*, 248—254.
TAYLOR, M. J. [1965]: The Gelation of Aqueous Bentonite Dispersions by Organic Ammonuim Ions. J. Appl. Chem. *15*, 512—518.
WADA, K. [1959]: Oriented Penetration of Ionic Compounds between the Silicate Layers of Halloysite. Amer. Mineralogist *44*, 153—165.
WEISS, A. [1961]: Eine Schichteinschlussverbindung von Kaolinit mit Harnstoff. Angew. Chemie *73*, 736.
WERNER, E. A. [1923]: The Chemistry of Urea. Longmans, London.

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MINERAL FACIES INVESTIGATIONS IN THE ALGYŐ-AREA

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SUMMARY

In the major part of the Algyő-area and in the southern part of the Danube—Tisza Interfluve the overwhelming majority of the basement complex under the Pannonian sediments is constituted by Variscian metamorphites of simple mineral composition in general. In the Algyő-area a sediment series of 2600 to 2800 metres thickness had developed during the Pliocene and Pleistocene periods. The temperature and pressure conditions reached only the thermal and pressure values of the methydric zone while they did not reach those of the diagenetic zone. This fact is proved by the existing mineral paragenesis. On the basis of the data calculated from the chemical composition of the Lower Pannonian basal conglomerates, sandstones and aleurites sampled from different depths, the *ACF* and *A'KF* triangular diagrams were drawn. On the basis of the projection points got in such a way the picture of the green schist facies of lower temperature became distinct and which contained quartz, albite, muscovite, biotite and chlorite as critical mineral and on this basis it is similar to the paragenesis of the *Abukuma-type*. In the *AFM* diagram chlorite covered nearly the same projection area than that of the literature data, while in case of biotite it is obvious that the members of this area are richer in Mg. The Lower Pannonian sediment series of several hundred metres thickness lying on the basement complex is the substance of the erosion area of nearly the same structure where, after deposition of the basal conglomerate, erosion of W-E direction is to be taken into consideration.

INTRODUCTION

In the axis of the hydrocarbon occurrence of the Szeged environs (Algyő) a buried metamorphic block range extends nearly in NW-SE direction. Its substances are metamorphites formed by Variscian metamorphism from older formations, i. e. mica schist with chlorite schist intercalations, quartzite, garnetiferous mica schist, gneiss and amphibolite. According to the data received so far in the position of the metamorphites certain zonality can be observed. These rocks determine for the most part the petrological structure of the so-called „basal conglomerate level" of Lower Pannonian age lying on the basement complex, and the mineral composition of the Lower Pannonian formations lying above them, to a certain extent. In the western side of the Algyő-structure and in the eastern part of the Deszk-area there occur such formations lying on the basement complex, which on the basis partly of their formations and partly of their fossils belong to the Upper Tortonian [BALOGH, 1968]. Therefore in the course of redeposition these detrital formations are to be taken into consideration to a certain extent.

CHARACTERISTICS OF THE LOWER PANNONIAN SEDIMENTS

In greater part of the Algyő-area there occur Lower Pannonian sediments of 400 to 600 metres thickness lying partly on the basement complex and partly on Upper Tortonian sediments. The lowermost member of this series is the „basal

conglomerate". This is not wide-spread, it is absent in the higher parts of the basement complex and is eroded from this place and wedges in the margins. The basal conglomerate level is, therefore, of varied thickness. This is not really a conglomerate which is proved by the facts that the grain-size over 2 mm diameter is of insignificant quantity, moreover, the coarse sand fraction (0.5 to 2.0 mm) hardly reaches one or two per cent. The measure of roundness is also very different. According to BÉRCZI [1970] the formation has to be regarded as lithoarenite. The basal conglomerate is composed of quartzite, mica schist, chlorite schist and of detritus of gneiss and amphibolite. As a result of this the quartz of undulatory extinction is frequent and which contains sometimes oriented inclusion series and in which twin of compression formed *(Fig. 1)*. Out of the microcline, orthoclase, plagioclase of dense twin-strips, muscovite, biotite and chlorite frequently of rutile inclusions can be found. In the pelitic substance kaolinite and illite occur out of the clay minerals.

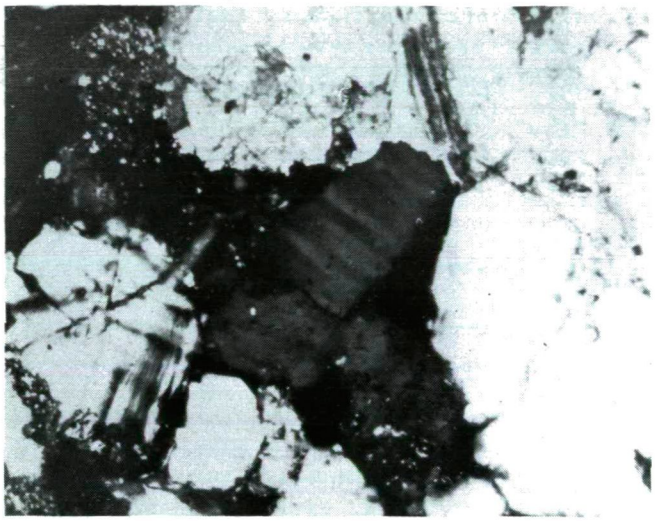

Fig. 1. Compression twin in quartz

The detritus of weathering coat being in the lower level, relates to the fact that first the decay cover redeposited and the erosion of the compact metamorphite followed this process. This process took place within a relatively short time, its detritus is assorted only to a small extent and assortment of certain size occurs in the uppermost part of this level, at most.

Above the Lower Pannonian basal conglomerate there is a grey, compact lime-marl level with varied transition zone. The sediment consisting of mainly chemical sediments is a calm-pelagic sediment series, which originated in a basin deepened sometimes under reductive conditions [BALOGH, 1969]. According to the X-ray diffractometric data of the insoluble residue of the rock treated by 2*N* hydrochloric acid it contains kaolinite, chlorite, muscovite, quartz and goethite. Due to the small grain-size rock-forming minerals could not be determined under microscope.

In the above-lying marly, clay-marly and sandstone-containing formation series fine-grained sandstones can be found which are reservoir-rocks of hydrocarbons.

The predominant grain-size is 0,1 to 0,2 mm which fact relates to rather good assortment. The bulk of the grains is quartz in several cases being of undulatory extinction. The rather frequent inclusion bands lie sometimes parallel with the rhombohedron planes, and are ordered sometimes parallel with the planes of the principal resp., secondary axes; in some grains compression twins also occur. Out of the feldspars orthoclase, microcline and plagioclase of polysynthetic twinning can be found. The quantity of feldspars is considerably less than that of the micas. The chlorite is of changing quantity, its quantity increases downwards, moreover, it can surpass the quantity of micas. The garnet, amphibole, zircon and apatite play insigni-

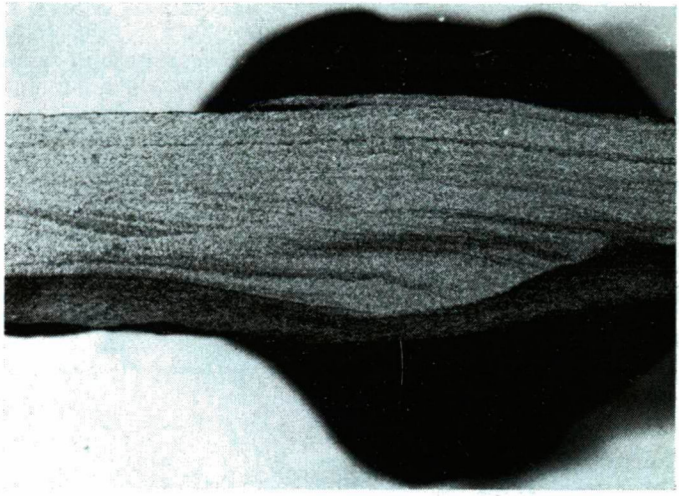

Fig. 2. Ripple mark in fine-grained sand

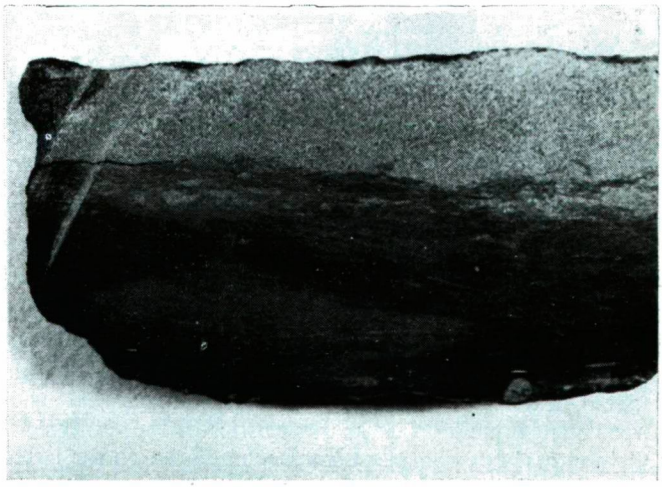

Fig. 3. Wedging aleurite in sandstone

ficant role, the two latter ones can be found mainly in form of inclusions. The cementing substance is carbonate which is calcite in the basal conglomerate level and calcite or dolomite in the layers above it.

The sandstones form thinner intercalations in the aleurite. These may show different textural and structural forms which may relate to their genetic conditions. In the fine-grained sandstone the buried ripple marks and cross-bedding *(Fig. 2)*, and in sandstone the wedging aleurite grains *(Fig. 3)* are frequent phenomena. In other cases fine-grained sandy strips are interbedded into aleurites *(Fig. 4)* but the sandstone and marl may also sharply be separated *(Fig. 5)*. In microscopic measures the desiccated hydrocarbons may cause micro-laminations *(Fig. 6)*. Coalificated plant remnants may cause band-forms, moreover, micas may abound also in strip.

The aleuritic parts of the formation relate to the deposition in calm water while sand intercalations indicate streaming water. In the Lower Pannonian strata these two factors play significant role in developing the different facies formations.

Fig. 4. Fine-grained sandy strips in aleurite

PRESSURE AND TEMPERATURE CONDITIONS IN THE LOWER PANNONIAN STRATA

According to the investigations during the Pliocene and Pleistocene periods sediments of 2.600 to 2.800 metres thickness originated in this area. The question is raised whether in this region such lithostatic pressure could exist, in the course of which, over the diagenesis, the metamorphism could begin or the anchimetamorphic zone could develop at least. The other question is that whether it would be possible to recognize some kind of characteristics of the mineral facies from the chemical composition of the detrital substance accumulated on the basement complex and whether any conclusion concerning the mineralogical-petrological facies conditions of the original rock could be drawn. This detrial substance derived either

directly from the basement complex or its detritus was several times transported and redeposited.

It is easy to answer first question. While in the Lower Pannonian sediments only the metamorphism connected to the subsidence took place, the thermal and pressure conditions as well as the critical minerals belonging to such metamorphism, are to be investigated.

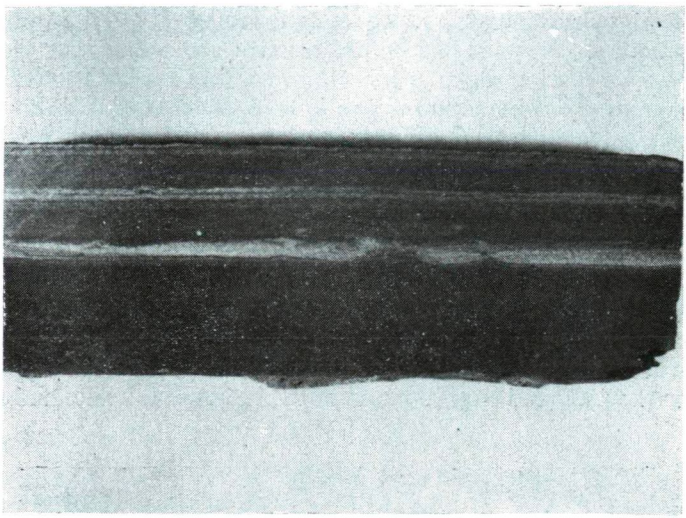

Fig. 5. Separation of sandstone and marl

According to the data of DANK [1965] and SOMFAI [1970] in the Lower Pannonian sediments of Algyő the pressure gives such values that overpressure is to be taken into consideration only in the level of basal conglomerate. This value is of about 25 per cent. The temperature values of these formations change between 90 to 156 centigrades depending first of all on the depth.

The Lower Pannonian sediments of Algyő lie in a depth of 2.000 metres in general, so they surpassed the pressure and temperature characteristics of the methydric zone. The diagenetic zone of deeper position corresponds to the position of the local sediments and the values of temperature do not exceed, too, the upper limit characteristic of this zone. As a result of this there is no clay mineral transformation. According to the investigations kaolinite and montmorillonite transform gradually into illite in the laumontite-prehnite facies. While kaolinite exists in the basal conglomerate level therefore no anchimetamorphic zone is probable. Temperature is also not high enough because the transformation of the clay minerals takes place at about 350 to 400° C and in consequence of this the lower limit of the facies may be put at this temperature value. The absence of the anchimetamorphic conditions is also proved by the fact that laumontite, prehnite as well as the secondary chlorite, albite and calcite are absent.

Finally it can be stated that in the Algyő-area the minerals of the Lower Pannonian strata proved to be the broken fragments of the original rock; and in the

course of subsidence no conditions could form under which the critical minerals could develop. This relates to the fact that the stability of the original minerals remained under the conditions mentioned above.

EVALUATION OF THE CHEMICAL ANALYSES (ACF, A'KF AND AFM DIAGRAMS)

In addition to microscopic, X-ray, DTA and TG investigations the chemical analyses were also used to determine the mineral facies, namely whether it would be possible to draw any conclusion concerning the mineral facies of the erosion area from the data of chemical analyses of the typical samples. The samples of the basal conglomerate level of different deep-borings and the aleurite and sandstone samples originating from the strata above it were used in selection of the samples instead of the classification of the Lower Pannonian published by KÖRÖSSY [1968].

It is well-known that the graphical demonstration of the minerals occurring in one facies is possible only in that case when the number of components determining the mineral's composition is not greater than the suitable numbers for geometrical demonstration. In the recently used triangular diagram of ESKOLA only three components can be taken into consideration. The only condition is that SiO_2 must give a surplus so its quantity should be negligible in the course of calculation. Our samples represent this case. The quantity of CO_2 was also neglected because it can be calculated informingly from the DTA and TG curves. These values may be assigned to the CaO and MgO content of calcite resp. dolomite and determining

Fig. 6. Desiccated hydrocarbon residue in sandstone

the CaO and MgO content bound by carbonates and subtracting this value from the original quantity of CaO and MgO, the remaining CaO and MgO quantities may be practically only in silicate bond. Magnetite and hematite were either absent or were represented only by insignificant quantities. Limonite, however, appeared several times in form of small globules and sometimes pyrite was found. When their quantity was measurable, corrections were applied. When garnet reached measu-

rable quantity correction was also used. In these cases the value of CaO was proportionally decreased in calculating the *A'*-value. Finally in addition to the alkalies the values of mole numbers calculated from the percentage of the weight of Al_2O_3, Fe_2O_3, FeO, MgO, MnO and CaO, were used.

While Al^{3+} and Fe^{3+} may replace isomorphously each other, therefore these values were summarized in the *A*-component and the quantity of alkalies was subtracted from it. Consequently, this value represents the Al_2O_3-quantity which is not bound to the feldspars. Though muscovite and biotite also contain a small

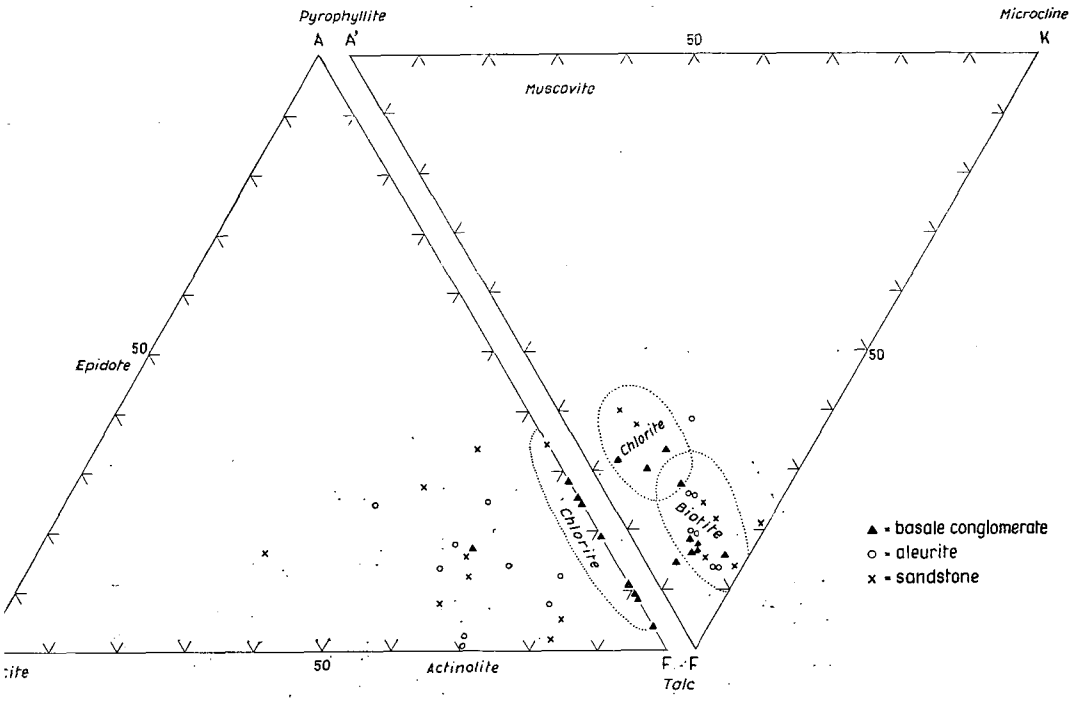

Fig. 7. Projection points, calculated from chemical analyses in the *ACF* and *A'KF* diagrams

quantity of H_2O, in our case this neglect of correction does not cause considerable error. The *C* value represents the quantity of CaO bound to silicates. While apatite is of insignificant quantity, it occurs sometimes in forms of inclusions, therefore the quantity of CaO connected to P_2O_5 can also be neglected. Finally, the *F* value represents the total quantity of $FeO + MnO + MgO$ bound to silicates.

The *A'KF* triangular diagram gives useful supplement to the *ACF* triangle. In this diagram the quantity and quality of the potassium-rich minerals is conspicuous. It is a common fact that this expresses also a mole-number relation and the correction of the accessory minerals is to be done as well. *A'* contains the Al_2O_3 quantity which is not bound to feldspars and the corresponding correction concerning the Ca-containing silicates (garnet, amphibole, epidote, etc.) is to be done. In our case only garnet occurs in several times. The *K* value corresponds to the mole-

cule number of K_2O and F, in comparison with the foregoing cases, indicates the total value of the molecule numbers of $FeO + MnO + MgO$.

Taking these facts into consideration the position of the single projection points deriving from the analytical data of the corresponding rock samples can be seen in *Fig. 7.*

From the *ACF* diagram it can be stated that projection points, deriving from the basal conglomerate level of different deep-borings, cover satisfactorily the place of chlorites in the *A—F* side. The projection points of the samples deriving from higher levels show certain deviations and this statement is true mainly of the sandstones. As a result of this the conclusion may be drawn that in the course of transportation the minerals being characteristic of the basal conglomerate became "diluted" to a certain extent and were mixed with other minerals. The fact can also be stated that in the neighbourhood of the projection points of the pyrophyllite, epidote and calcite the projection points are absolutely absent. In the samples investigated these minerals could be detected neither by microscopic nor by X-ray investigations, neither in the basal conglomerate level nor in the strata above it.

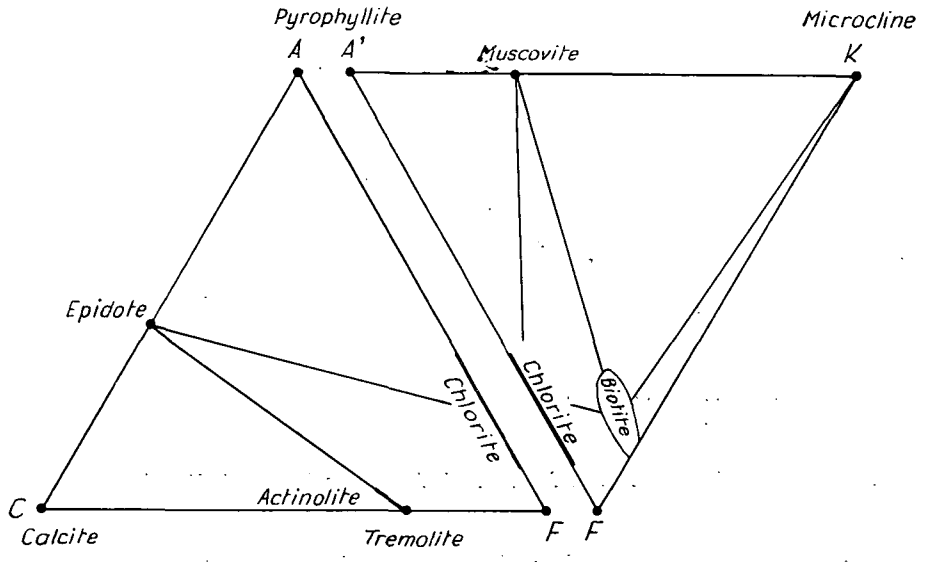

Fig. 8. ACF and *A'KF* diagrams of the greenschist facies of Abukuma type

The *A'KF* diagram demonstrates excellently the predominating role of biotite and chlorite. Independently of the depth and rock type (basal conglomerate, aleurite, sandstone) no greater deviations can be found; therefore the same conclusion can be drawn, i. e. that the sediment derives from an area of nearly the same geological structure. The only difference is that the ratio of the minerals to one another changes to smaller or greater extent but the same variety remains. If there would be any deviation this may be concerned to the sandstones of the higher levels.

When comparing the *ACF* and *A'KF* triangle diagrams of the green schist

facies to those of ESKOLA's plotting it is obvious that there is great conformity with the projection areas derived from the chemical data of the Algyő samples *(Fig. 8)*. Im the *ACF* diagram the projection area of chlorites show a good conformity and in the *A'KF* diagram, however, the projection areas of biotite and chlorite nearly cover each other.

In the *ACF* and *A'KF* diagram the projection points are in keeping with the paragenesis of the *Abukuma type*. This type represents a regionally developed series which formed under relatively low pressure. The temperature is about 700° C, *i. e.* it is a more heated part of the crust and the formation could take place in a depth of 8 to 11 kilometres. In case of this metamorphic series a green schist facies of lower temperature and an amphibolite facies endured larger-scale metamorphism, can be distinguished. In the subfacies of the green schist facies the typomorphic minerals are the quartz-albite-muscovite-biotite-chlorite and quartz-albite-biotite, respectively. The boundary of the green schist and amphibolite facies is represented by the disappearance of chlorite and by the appearance of new minerals, i. e. diopside, grossularite/andradite and staurolite. The typomorphic minerals of the green schist facies relate to the fact that in the overwhelming majority of the basement complex the metamorphism did not get an equilibrial stage in contrary to the metamorphites of the other regions of the Great Hungarian Plain [SZEPESHÁZI, 1968, SZÁDECZKY-KARDOSS *et al.* 1969].

Taking into consideration the possibilities of the *Barrow series* (which can be characterized by a paragenesis representing higher pressure values) it can be stated that the appearance of chlorite is only accidental while it is characteristic of the Algyő-area. The absence of cordierite, kyanite and staurolite relates at the same time to the fact that any green schist type of this series is investigated, it cannot be identified with that of the Algyő-area. Further, the amphibolite facies also could not form and this is proved either by the typomorphic minerals of the *Barrow* or by those of the *Abukuma type*. The absence of the stilpnomelane and epidote in the typomorphic minerals excludes the possibility of existence of the green schist facies of *Barrow type*.

In the *ACF* and *A'KF* diagrams the component *F* contains the quantity of FeO(MnO) + MgO. Though FeO and MgO may replace each other isomorphously, the measure of replacement may be different in the FeO- and MgO-containing silicates occurring in the rocks. Among others this measure depends on the chemism of the magma and associated rock as well as on the pressure and temperature. Theoretically FeO and MgO are two independent components of the system and could not be replaced by each other. The *AFM* diagram was developed by THOMPSON [1957] where *A* denotes Al_2O_3, *F* is the FeO and *M* is the MgO.

In the *AFM* diagram it is possible to plot a paragenesis depending on the chemism which developed from pelitic sediments as a result of metamorphism. In this case the metamorphite always contains quartz except several examples. Due to the high silification degree the plotting of those may be neglected. The plotting of H_2O is also negligible in those cases in which the pelitic sediments were metamorphized, for example in case of the basement complex of the Algyő-environs.

The pelitic sediments and their metamorphites can be characterized by the system of nearly SiO_2—Al_2O_3—MgO—FeO—K_2O—H_2O composition, when TiO_2 and Fe_2O_3 are bound mainly to biotite, Na_2O to alkaline feldspar and CaO to plagioclase and almandine, respectively. While on the basis of the afore-mentioned facts the quantities of SiO_2 and H_2O are negligible, the number of components of a quartz-contain-

ing metamorphite decreases to four components: Al_2O_3, MgO, FeO, K_2O. As a result of this the composition can be demonstrated in a tetrahedron. From the plotting point of view it is advantageous to investigate the side of the tetrahedron on which Al_2O_3, FeO and MgO are plotted. In this side the K_2O-less minerals, i. e. chlorite, chloritoide, pyrophyllite, the Al_2SiO_5 varieties as well as staurolite, almandine and cordierite can be found. The K_2O-containing minerals, i. e. biotite and stilpnomelane are in the tetrahedron and their projection points are outside the tetrahedron, on the lengthening of the plane. The position of the projection points can be derived from the molecule number calculated from the percentage of weight, on the basis of the following formula:

$$A = \frac{Al_2O_3 - 3K_2O}{Al_2O_3 - 3K_2O + MgO + FeO} \quad \text{and} \quad M = \frac{MgO}{MgO + FeO}$$

Fig. 9 shows the position of the projection points resulted from these formulae. It is obvious from the results that biotite originating from the metamorphite of Algyő deviates from the literature's data in average value MgO/(MgO + FeO), which is 0,6, in our case it falls between 0,6 to 0,8 and first of all the samples of the

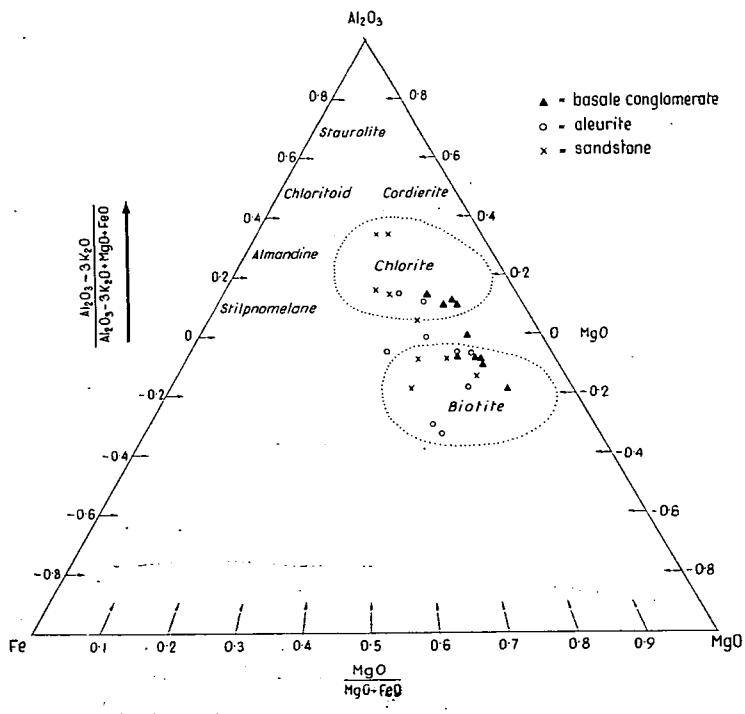

Fig. 9. Projection points calculated from analyses in the *AFM* diagram.

basal conglomerate level are poorer in MgO. The projection points of the chlorites originating from the same samples agree excellently with the values of literature data. From the diagram it is obvious, however, that the substance of the erosion area

of nearly the same structure accumulated in the investigated series of 200 to 300 metres depth. In the paragenesis, of course, quartz and chlorite occur in addition to biotite and muscovite which is also proved by the facts mentioned above.

PALEOGEOGRAPHIC CONDITIONS

At the end of the Paleozoic era the surroundings of Szeged and the Danube-Tisza Interfluve had been an uplifting and strongly eroding continent for a long time. The products of erosion got the farther-lying sedimentary basins hence the younger sediments deposited on the basement consisting of old metamorphic rocks, in general [SZEPESHÁZI, 1968]. The overwhelming majority of the basement is an unbalanced metamorphite of simple mineral composition, in general. SZÁDECZKY-KARDOSS *et al.* [1969] related to the fact that in the Szeged-environs there are greenschist and chlorite-schist, respectively. On the basis of the investigations of the absolute geochronology in this area predominantly epi-mesozonal Variscian metamorphism, while in the farther-lying areas retrogressive Alpine metamorphism (chloritization of biotite, sericitization of feldspars) can be observed. According to JUHÁSZ [1969] the overwhelming majority of the metamorphites of the basement complex in the Danube-Tisza Interfluve is a paragenesis which did not reach the equilibrial stage.

In the history of evolution of the sedimentary basins KÖRÖSSY [1970] distinguishes two great sedimentation cycles in the Neogene basins. The first cycle is the Burdigalian-Helvetian marine cycle in the Miocene, the second is the cycle during the Pliocene which may be assigned to the Lower Pannonian. The two cycles are separated from each other by the pre-Pontian erosion in the Sarmatian and Lower Pannonian [SZÁDECZKY-KARDOSS, 1938]. Since the Neogene the stabilized basin floor has moved only vertically and began to subside in the Pliocene. The measure of this subsidence locally surpasses the 3.000 metres [KÖRÖSSY, 1963].

Taking into consideration the position of the Upper Tortonian formations of the Algyő-area it is to be supposed that if the metamorphic range emerged from the sea it did not reach greater heights. This may explain the appearance of the Miocene formations east of Deszk. In this case after the transgression of the Upper Tortonian and before or during that of the Lower Pannonian there ought to be an uplifting surface and this phenomenon may explain the absence both of the Upper Tortonian and the basal conglomerate on the tops of the basement complex. This presumption may also be explained by the observation that lower products of the lower basal conglomerate level are metamorphites of weathering coat and this means the redeposition of the covering strata. The direction of origin of the transgressive sediment cannot be unambiguously determined. The S—N erosion direction is presumable but it had to change within a short time. The NW—SE direction is also probable; this may be proved by the fact that due to the higher chlorite content of the more sandy part of the slightly assorted sediment, accumulated in consequence of the rapid erosion, is of greenish-grey colour in the deep-boring of A-50, 52, 55 and 91. This fact grants the presumption that in the deep-borings of A-71 and 89, lying northwestwards from these in a higher level, the substance of the basement complex is albitic chlorite-schist which had been eroded and could cause the greater quantity of chlorite.

After deposition of the transgressive conglomerate the erosion of WNW direction is more probable. In this direction the mineral composition of the rocks

of the basement complex is similar to that of the sandstones and aleurites above the basal conglomerate. This may also be proved by the fact in the half part of the core of the deep-boring No. 107 *Foraminifera sp.* occurs. Hence it is absent in the Lower Pannonian, it could be redeposited only from the Miocene sediments of the Ásott-halom-environs of higher position (it is plotted in this form also on the map of KÖRÖSSY, 1970). In this deep-boring the above-mentioned core part is in a height of 480 metres above the basement complex, therefore it could not derive from the area of the Deszk-environs but only from the West. There was also considerable relief difference between the Algyő-area and the western part.

Finally it can be stated that after the deposition of the Lower Pannonian transgressive basal conglomerate the Algyő area subsided gradually. The transportation of the clastic sediment was directed into this basin from the west and this process continued during a longer space of time. These are the reasons while the relatively thick sediments of nearly the same character accumulated in this area.

REFERENCES

BALLA, K. [1965]: Az üllési kutatási terület mélyföldtani ismertetése. — Földt. Közl., **95**, p. 190.

BÁRDOSSY, GY., MESKÓ, L., PÓKA, T., SAJGÓ, CS., TOMSCHEY, O. [1970]: Sedimentpetrographische Untersuchung der tertiären Gesteine des Algyőer Gebietes. — Acta Geol. **14**, p. 251.

BÉRCZI, I. [1970]: Sedimentological investigation of the Algyő hydrocarbon-holding structure. — Acta Geol., Acad. Sci. Hung., **14**, p. 287.

BARTH, T. F. W., CORRENS, C. W., ESKOLA, P. [1939]: Die Entstehung der Gesteine. Berlin.

CSIKI, G. [1963]: A Duna—Tisza köze mélyszerkezeti és ősföldrajzi viszonyai. — Földr. Közl. **87**, p. 19.

DANK, V. [1963]: A dél-alföldi neogén medencék rétegtani viszonyai és kapcsolatuk a dél-baranyai és jugoszláviai területekhez. — Stratigraphy of the Neogene basins of Southern Alföld and their relation to the areas of South Baranya and Yugoslavia. — Földt. Közl. **93**, p. 304.

DANK, V. [1965]: A dél-alföldi neogén medencerészek mélyszerkezeti viszonyai és kapcsolatuk a dél-baranyai és jugoszláviai területekel. — Deep structural patterns of the Neogenic basin portions of the southern Great Plain and their relation of the areas of South Baranya and Yugoslavia. — Földt. Közl. **95**, p. 123.

DANK, V. [1965]: A dél-alföldi szénhidrogén kutatások legújabb eredményei. — Földt. Kutatás VIII, 4, p. 1.

DANK, V., BÁN, Á. [1966]: Az algyői kőolaj és földgázelőfordulás földtani viszonyai és termeltetésének elvei. — Földt. Kutatás 1966. évi különszáma.

JATE Földtani Tanszék [1966]: Dél-magyarországi (Szeged környéki) neogén medencerész földtani fejlődéstörténete. Manuscript, in Hungarian.

JATE Földtani Tanszék [1969]: Bevezetés néhány törmelékes üledékfácies vizsgálatába. Manuscript, in Hungarian.

JATE Ásványtani, Geokémiai és Kőzettani Tanszék [1970]: Szénhidrogéntároló üledékes kőzetek komplex geokémiai vizsgálata. Manuscript, in Hungarian.

JUHÁSZ, Á. [1966]: Szank és környékének harmadidőszaknál idősebb képződményei. — Vorteriäre geologische Bildungen von Szank und Ungebung. — Földt. Közl., **96**, p. 427.

JUHÁSZ, Á. [1969]: A Duna—Tisza köze mélységi, magmás és metamorf képződményei. — The crystalline rocks of the Danube—Tisza Interfluve. — Földt. Közl., 99, p. 320.

KÖRÖSSY, L. [1963]: Magyarország medence területeinek összehasonlító földtani szerkezete. — Comparison between the geological structure of the basin regions of Hungary. — Földt. Közl., 93, p. 153.

KÖRÖSSY, L. [1968]: Entwicklungsgeschichtliche und paläogeographische Grundzüge der ungarischen Unterpannons. — Acta Geol. Acad. Sci. Hung., 12, p., 199.

KÖRÖSSY, L. [1970]: Entwicklungsgeschichte der neogenen Becken in Ungarn. — Acta Geol. Acad. Sci. Hung., **14**, p. 421.

Magyarország szénhidrogén telepei. Algyő. 1970. Országos Kőolaj és Gázipari Tröszt. Budapest.

SOMFAI, A. [1970]: Examination of overpressure reservoirs in the Great Hungarian Plain; a classification of the causes of overpressure. — Acta Miner. Petr., XIX. 2. p. 173.

Szádeczky-Kardoss, E., Juhász, Á., Balázs, E. [1969]: Erläuterung zur Karte der Metamorphite von Ungarn. — Acta Geol. Acad. Sci. Hung., **13**, p. 27.
Szepesházi, K. [1968]: A kristályos aljzat fontosabb típusai a Duna—Tisza köze középső és déli részén. — MÁFI Évi jelentése 1966. évről, p. 275.
Winkler, H. G. F. [1967]: Die Genese der metamorphen Gesteine. Berlin—Heidelberg—New York.

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STUDY OF THE DISTRIBUTION OF TRACE ELEMENTS IN THE ROCKS OF NUGGIHALLI SCHIST BELT, HASSAN DISTRICT, MYSORE STATE, INDIA

C. NAGANNA and S. G. PHENE

ABSTRACT

Semi-quantitative spectrochemical analyses of the rocks representing the three major lithological units of the Nuggihalli schist belt, namely the ultrabasic rocks, the green schists, and the amphibolites have been done. Based on the distribution of elements like Cr, Ni, Cu, Co, V, Ti and B, the amphibolites of this region are considered to be ortho-amphibolites formed after the pre-existing igneous rocks of doleritic or basaltic composition. Further, by a comparison of the nature of distribution of these elements in the three major rock units, it is inferred that the green schists are derived from the alteration of ultrabasic rock and there has not been any differentiation in the rocks of this region.

INTRODUCTION

Attempts are being made in recent years to use the study of trace element distribution for solving geological problems. ENGEL and ENGEL [1951, 1953, 1962], EVANS and LEAKE [1960], SHAW and KUDO [1965], TUREKIAN [1965] are some of the people who have made important contributions in this field. Opinion is divided among geologists about the usefulness of this method. However, in certain cases where the conventional methods fail, this method of study is regarded as important. In the present investigation it is seen that rock units like ultrabasics, green schists, and amphibolites are being involved in a peculiar geological setting in Nuggihalli schist belt. By conventional studies it is rather difficult to establish the relationship existing between these rock units. Therefor, an attempt has been made to trace the relationship among these rock units of this region by a semiquantitative spectrochemical analyses and its interpretation.

GEOLOGICAL SETTING

The name Nuggihalli schist belt is given to a narrow strip of Dharwarian (Pre-cambrian) schistose rocks occurring in the vicinity of Nuggihalli, (Lat. 13° 1', Long. 76° 28'), Hassan District with NNW-SSE strike and varying amounts of dip. This schist belt is surrounded by granites and granite gneisses. The belt chiefly consists of *(a)* the ultrabasic rocks, represented by dunite, pyroxenite and serpentinite; *(b)* green schists made up of chlorite schist, talc chlorite schist, talc actinolite schist, talc kaemmererite schists, etc. and *(c)* amphibolites. In the field the ultrabasic rocks appear to intrude into the amphibolites. The green schists are between the amphibolites and the ultrabasics. Though the ultrabasics appear to grade on to the green schists, and no such gradation is seen between the amphibolites and the green schists, the field characters are not very clear to indicate the relationship among these rocks.

SPECTROCHEMICAL ANALYSES AND ITS INTERPRETATION

Thoroughly homogenized samples of 12 rocks representing all the three lithological units were subjected to spectrochemical analyses. The semiquantitative estimation of the lines were made using the charts prepared by KALININ *et al* [1952]. During the semiquantitative estimation elements like Si, Mg, Cr, Ni, Mn, Cu, Co, Al, V, Ca, Ti and B have given positive results whereas elements like Be, As, Ba, Ge, Sb, Pb, Sn, Pt, Mo, Ag, Cl, Zn, Bi and Se have given negative results. The results of the estimation are given in Table I.

A general survey of the results of the spectrochemical analyses given in Table I indicates that the trace element content in these rocks are slightly lower than the arithmetic mean of these elements in the basic igneous rocks reported by EVANS and LEAKE [1960]. However, they appear to fall well within the range of variations for the basic igneous rocks.

TABLE I

Trace element content of rocks from Nuggihalli schist belt

Elements	A_1	A_2	A_3	A_4	U_1	U_2	U_3	U_4	G_1	G_2	G_3	G_4
Si	6	6	6	6	6	6	6	6	6	6	6	6
Cr	2	1	—	1	2	3	1	2	2	5	—	1
Ni	3	2	2	3	4	4	4	3	3	4	2	3
Mn	4	3	3	4	3	4	4	4	4	3	2	1
Cu	2	2	2	2	1	1	1	2	1	1	1	1
Co	1	1	1	2	2	3	3	3	1	3	1	2
Al	4	4	5	4	1	2	2	3	3	5	6	5
V	1	1	2	1	—	—	—	—	—	—	—	—
Mg	6	6	6	6	6	6	6	6	6	5	6	6
Ca	5	5	5	5	2	1	1	5	4	2	4	3
Ti	1	1	2	1	—	—	1	1	1	5	2	1
B	1	—	—	—	1	2	2	1	1	2	1	—

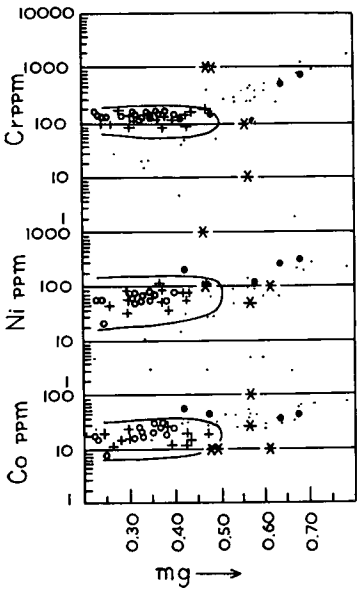
A_1 to A_4 — Amphibolites
U_1 to U_4 — Ultrabasics
G_1 to G_4 — Greenschists

6 — X0.00%
5 — X.00%
4 — X.00—0.X0%
3 — 0.X0—0.0X%
2 — 0.0X—0.00X%
1 — 0.00X%

In the amphibolites there is no variation in Si, Cu, Ca, Mg, Cr and V. Cr is poor in all the types and is absent in one of the amphibolites. Significantly B is absent in all the amphibolites except in one which has a slightly different setting than the other amphibolites. This amphibolite A_1 makes a direct contact with the ultrabasics in the field.

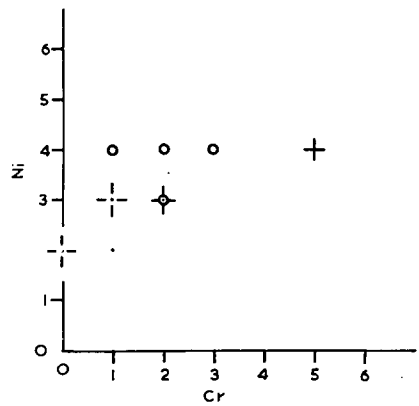
LEAKE [1964] has made use of the elements like Cr, Ni, Co and Cu in amphibolites for distinguishing ortho-from para-amphibolites. By plotting Mg against Cr, Ni, Co and Cu for the Karroo dolerites, ortho-amphibolites, pelites, etc. LEAKE (op. cit.) has demarkated fields for rocks of igneous parentage. This figure is reproduced in *Fig. 1* with the plots for the amphibolites from Nuggihalli. It is seen in

this figure that the plots for the amphibolites from Nuggihalli correspond to Karroo dolerites and Langy ortho-amphibolites, thereby suggesting that the amphibolites under study are ortho-amphibolites probably formed after the pre-existing igneous rocks of doleritic or basaltic composition.



o-CONNEMARA PELITES +-LITTLETON PELITES
· KAROO DOLERITES
•-LANGØY ORTHO-AMPHIBOLITES
* AMPHIBOLITES FROM NUGGIHALLI SCHIST BELT

FIG: 1



THE PLOTS OF Ni AGAINST Cr IN AMPHIBOLITES, ULTRABASICS & GREEN SCHISTS IN NUGGIHALLI SCHIST BELT

FIG: 2

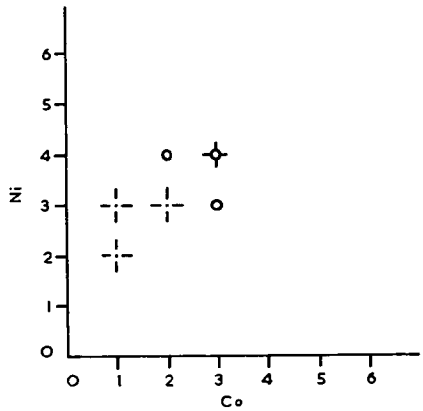
Among the ultrabasic rocks one specimen of dunite, two specimens of serpentinites and one specimen of pyroxenite have been analysed (Table I). In these rocks, Cr, Ni, Mn, Cu, Co and Al vary from rock to rock. Vanadium is absent in all the rocks. Boron which is absent in the amphibolites except in one, is present in all the ultrabasic rocks. The content of B is more in the two serpentinites. This may be due to the formation of serpentinites from dunite through autometamorphic processes.

In order to know whether there is any trend of differentiation among these rocks and also among the rocks of the other lithological units of this area, the value of Cr, Ni and Co are plotted against each other and shown in *Figs. 2* to *4*.

In these figures it can be seen that not only the plots for the ultrabasic rocks are scattered but also the plots for the rocks of the three major rock units are non-aligned. This shows that there is no differentiation among the rocks of this area.

In the green schists there is considerable variation in the content of Cr, Ni, Mn, Co, Al, Ca, Ti and B. Vanadium, which is present in the amphibolites, is absent here. Except in talc schist G_4, B is present in the other three. Since the green schists

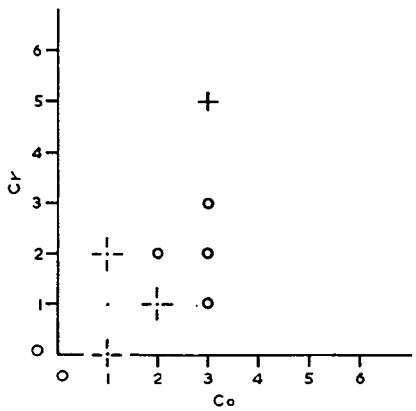
are developed in between the amphibolites and the ultrabasic rock, it is possible that they might have been formed after either of the two. EWANS and LEAKE (op. cit.) have selected elements like Cr, Ni, Co, Cu, Zr, Se, Sr and B as characteristic elements which would show a pronounced variation in their content in rocks depending upon the parent material from which the rocks are derived. The content of these elements in rocks of the three lithological units are represented in histograms in *Fig. 5*. An



THE PLOTS OF Ni AGAINST Co IN AMPHIBOLITES, ULTRABASICS & GREEN SCHISTS IN NUGGIHALLI SCHIST BELT

•-AMPHIBOLITES O-ULTRABASICS + GREEN SCHISTS

FIG: 3



THE PLOTS OF Cr AGAINST Co IN AMPHIBOLITES, ULTRABASICS & GREEN SCHISTS IN NUGGIHALLI SCHIST BELT

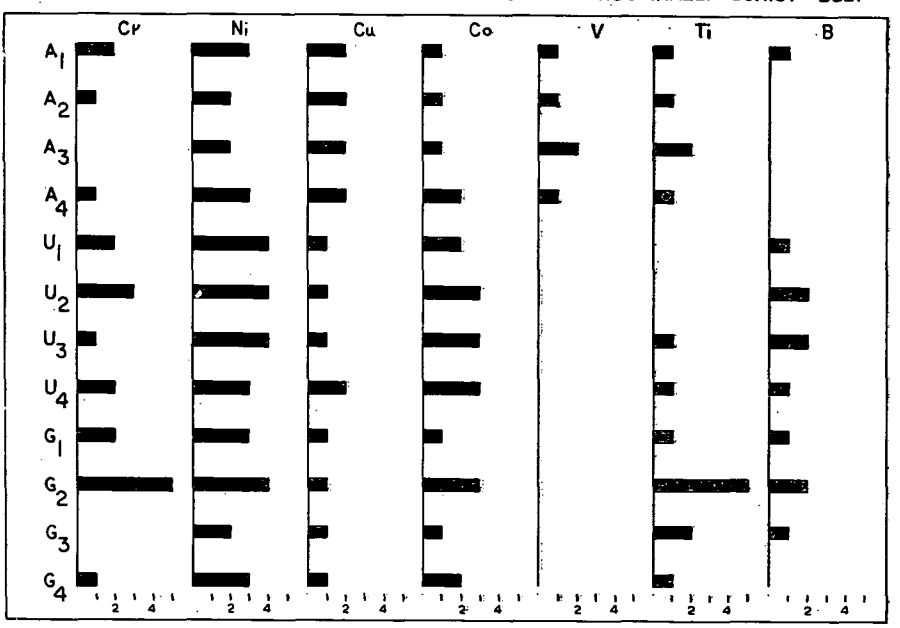
FIG: 4

inspection of the histograms shows a marked similarity in the distribution of the characteristic elements in ultrabasics and the green schists and these in turn are dissimilar to the distribution in the amphibolites. From this it can be inferred that the green schists are formed after the ultrabasics.

CONCLUSION

From the present study it can be concluded that the distribution pattern of the trace elements in the rocks of Nuggihalli schist belt conform to the pattern of distribution of these elements in basic igneous rocks reported by EVANS and LEAKE (op. cit.). Based on this distribution it is also concluded that the amphibolites of this region are ortho-amphibolites formed after the pre-existing basic igneous rocks of doleritic or basaltic composition. The study shows that there is no differentiation, either among the rocks of individual lithological units or among the members of the major lithological groups. Further, the study indicates that the amphibolites have no genetic relationship with the ultrabasic rocks and the green schists, while green schists appear to have been derived from the ultrabasics.

HISTOGRAMS REPRESENTING THE DISTRIBUTION OF CERTAIN CHARACTERISTIC TRACE ELEMENTS IN THE MAJOR ROCK TYPES OF NUGGIHALLI SCHIST BELT



1=< 0.001%. 2 = 0.001 - 0.01 %. 3 = 0.01 - 0.10 % .4 = 0.10 - 1.00 % A = AMPHIBOLITES
U ULTRABASICS G GREEN SCHISTS

FIG: 5

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REFERENCES

ENGEL, A. E. J. and ENGEL, C. G. [1951]: Origin and evolution of hornblende-andesine amphibolites and kindred facies (abstract). — Bull. Geol. Soc. Amer. **62**, p. 1435.

ENGEL, A. E. J. and ENGEL, C. G. [1953]: Greenville series in the northwest Adirondack Mountains, New York, Part I, General features of the Greenville Series. — Geol. Soc. America, Bull., **64**, pp. 1013—1947.

ENGEL, A. E. J. and ENGEL, C. G. [1962]: Progressive metamorphism of amphibolites, NW Adirondacks mts. New York, Petrological Studies. — Buddington volume, Geol. Soc. Am. Bull. pp. 37—82.

EVANS, B. W. and LEAKE, B. E. [1960]: The composition and origin of the striped amphibolites of Connemara, Ireland. — Jour. Petr. **1**, pp. 337—63.

KALININ, S. K., JARNEL, M. A., ALESKSEEVA, A. I. and NAJMAIK, L. C. [1952]: Atlas spektralnych linij Moscow.

LEAKE, B. E. [1964]: The chemical distinction between ortho- and para-amphibolites. — Jour. Petr. **5**, 238—254.

SHAW, D. M. and KUDO, A. M. [1965]: A test of the discriminant function in the amphibolite problem. — Min. Mag. **34**, pp. 423—435.

TUREKIAN, K. K. [1963]: The use of trace element geochemistry in solving geologic problems. Studies in Analytical Geochemistry. Roy. Soc. Canada Publication — 6.

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QUARTZ DIORITE FROM WATER-EXPLORATORY DRILLING AT BALATONFENYVES

L. RAVASZ-BARANYAI and Cs. RAVASZ

The water-exploratory hole drilled in 1969 in Balatonfenyves village, Transdanubia, Hungary, reached at 601.0 m depth the pre-Tertiary basement under younger basin sediments, to stop then at 603.0 m in an intrusive magmatic rock, identified macroscopically as of granitoid type, microscopically as quartz diorite, the first rock of this kind ever found in Transdanubia.

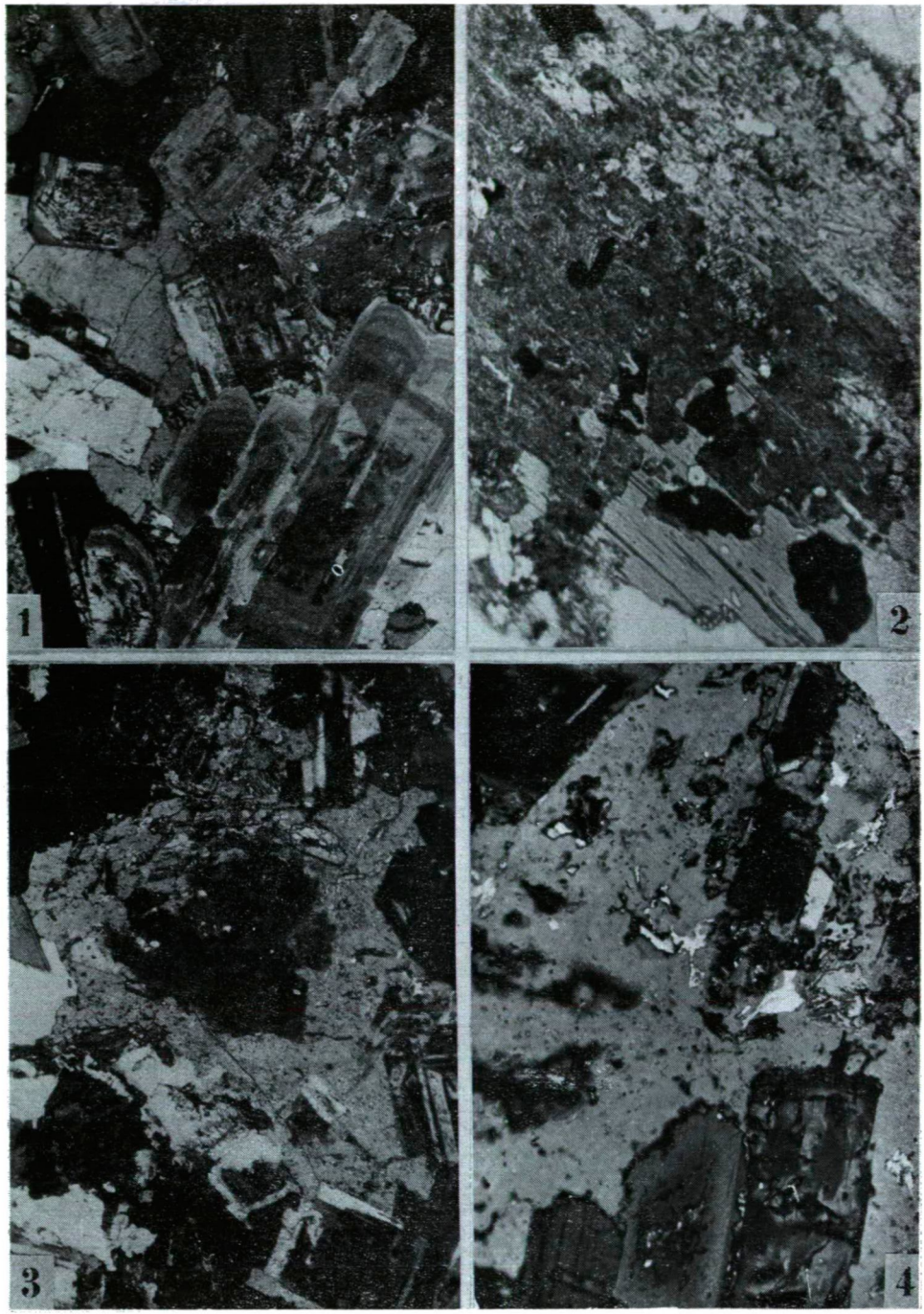
The fresh rock is medium-gray, of medium grain size, showing a holocrystalline texture constituted by euhedral to anhedral grains. Main constituents of its mineralogical composition are intermediate plagioclase, quartz, hornblende, biotite, potash felspar. Accessories: ilmenite, sphene, apatite, zircon, sporadical magnetite and garnet. Secondary (autohydrated) minerals: grammatite (tremolite), anatase, calcite and some chlorite.

Volumetric % of the components as found with the integration stage:

Plagioclase	50.4%
Quartz	21.6
Hornblende— (grammatite)*	10.4
Biotite— (chlorite)*	9.0
Potash feldspar	7.8
Accessories	0.8
	100.0%

A predominant main constituent of the rock, plagioclase is idiomorphic to hypidiomorphic, with advanced zoning *(Fig. 1)*. As a rule, the inner core is of most basic composition, whereas the outer rims are more acidic, though the phenomenon of recurrence is also common. The plagioclase crystals are twinned according to the albite, pericline and Carlsbad laws, complex twins being frequent. Changing in composition even within one crystal, plagioclase can be considered to span the interval between basic oligoclase (An_{25}) and labradorite (An_{60}). Most common are the crystals showing a composition corresponding to andesine ($An_{37\cdot5}$). No more than some 2% of the crystal individuals are oligoclase; a corresponding composition can often be measured on the outer rims of zoned plagioclases. On the

* In measurements with the integration stage secondary calcite was included in amphibole group, since calcite is present as a replacement of amphiboles. Chlorite was measured together with biotite.


1
2
3
4

extinction angles data measured by *Michel-Lévy*'s method and on complex twins (combination of Carlsbad and albite twins) it is the value $An_{42\cdot5}$ that can be considered the subaverage composition of plagioclases.

The mafic minerals are represented by biotite and hornblende. Biotite is fresh, of light to dark brown pleochroism, zircon inclusions being surrounded by pleochroic halo. Hornblende is represented by a green variety. In the majority of the cases it occurs together with an actinolitic alteration product: finely fibrous grammatite crystal aggregates forming large, irregularly outlined patches *(Fig. 2)*. The presence of this characteristic Ca-amphibole of the actinolite group is evidenced by the X-ray diffractogram showing a peak of 8.38 *d* value occurring beside the 8.50 Å reflexion of hornblende and having nearly the same intensity. The formation of grammatite can be explained by the uralitization of an earlier diopsidic pyroxene, by its autohydrothermal alteration. However, the presence of diopsidic pyroxene or diopside in this type can be ascribed to the phenomenon of contamination only. Affected by subsequent CO_2 metasomatism of lower degree, grammatite has been partly carbonatized. Biotite, hornblende and grammatite combine to form crystal groups in the rock, frequently containing apatite inclusions and minute ilmenite-anatase--leucoxene crystals.

In most of the cases, anatase — coupled with leucoxene — can be observed around an ilmenite nucleus and it may be supposed to be an alteration product of sphene, a hypothesis suggested by the sphenic form of the anatase crystals still recognizable in some places. Like the pyroxene seemingly present on account of grammatite, the sphene rimming the ilmenite cores warrants the contaminated character of the rock. The formation of anatase deduceable from sphene can be ascribed to autohydration that must have affected the rock.

Quartz and potash feldspar are xenomorphic in the rock. The quartz shows a slightly undulated extinction, submicroscopic inclusions are frequently present.

Potash feldspar is poor, no perthitic intergrowth can be observed to occur. The homogenity of the mineral is broken by abundant inclusions represented by remnants of plagioclase, hornblende, chlorite, calcite and quartz crystals as well as by larger masses of submicroscopic inclusions (Fig. 3, 4). Viewed under the microscope with crossed nicols, even the inclusion-free parts of certain crystals are not entirely homogeneous, showing irregular patches, vein-like features, 0,03—0,1 mm in size, of different extinction. In case of some microscopic patches, at high magnification, some imperfect, polysynthetic twinning hardly recognizable, is manifested. In order to study potash feldspar at closer scrutiny, the authors performed measurements with the universal stage, to determine both the optic angle and optical orientation, varying in dependence on the degree of Al/Si order. In doing so they used a conoscopic method by the aid of producing interference figure of measuring $2V_\alpha$. The results allow the authors to conclude that $2V_\alpha$ varies from crystal to crystal and even within one and the same crystal, the range of variation being comparatively large: 40—47°. The authors have tried to measure optic angle (by

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Fig. 1. Texture of quartz diorite. X N, 68×.

Fig. 2. Hornblende, biotite (lower part) and irregular crystal aggregates of fibrous grammatite. Inclusions: apatite, anatase-, leucoxene (dark). II N, 68×.

Fig. 3. Xenomorphic potash feldspar crystals containing numerous inclusions. X N, 28×.

Fig. 4. Plagioclase crystal showing resolved and corroded rim. X N, 68×.

the extinction method) even for the minor single patches, still measurable. The value thus obtained has been about 60°. The plane of the optic axes is perpendicular or nearly perpendicular to (010). In according to the optical orientation potash feldspar is monoclinic while the above-mentioned patches within the crystals seem to turn into triclinic symmetry. On the strength of optical properties potash feldspar is of disordered structure or shows some slight to fair degree of Al/Si order which tends to increase in the single microscopic patches. According to the X-ray diffractogram (a powder diagram made of the separated potash feldspar fraction of the rock), the triclinicity of potash feldspar is 0. 0. Measured on the basis of the position of the ($\bar{2}01$) reflexion by the use of the *Bowen-Tuttle* diagram, the Or content of potash feldspar equals 88%. *Wright*'s diagram, based upon 2 θ (060), $-(204)$, $-(201)$, yields the same result. In addition, it can be stated that the examined potash feldspar is of low albite content and has its plotted dot between the high sanidine and the maximum microcline. As shown by the chemical analyses of the potash feldspar fraction separated by heavy liquids by means of centrifuging, potash feldspar has the following average composition: $Or_{88\cdot2}$, $Ab_{11\cdot7}$, $An_{0\cdot1}$. With Tuttle's diagram the average of 2 $V\alpha$ yielded a value of about Or_{88}. According to the above data, the potash feldspar under consideration is a cryptoperthitic orthoclase (even though no definite agreement concerning the nomenclature of potash feldspars could so far be reached). The lack, or low to medium degree, of Al/Si order suggests rapid crystallization, i. e. a rapid cooling down of the system. To determine with higher accuracy the temperature of the unstable crystallization of potash feldspar, known to crystallize for the most part at a penumatolytic temperature, would be difficult because of the manifold influences involved under the given circumstances: a fact notified also by I. M. SÁENZ [1967]. It is probable, however, that the final crystallization phase of potash feldspar has fallen in the hydrothermal temperature range already. Resolution of the already solid crystals by the pneumatolytic-hydrothermal solutions can be observed even under the microscope *(Fig. 4)*. During this process the $Or\text{-}Ab + An$ ratio may also have been changed with regard to the total of the crystal in some minor patches around the mineral inclusions within the crystal. At the same time, during partial re-solution a partial re-crystallization of potash feldspar can be supposed to have taken place, a phenomenon confined to the microscopic patches just mentioned. The observed optical divergences of the individual potash feldspar crystals may be explained by the above processes.

Nomenclaturally, in the sense of *Lindgren*'s definition, the rock is quartz diorite (tonalite), as the weight % quantity of potash feldspar is $< 13^1/_3$. JOHANNSEN showed the nomenclatural boundary of granodiorite to quartz diorite to lie at 5% potash feldspar. In other words, he assigned to this category those rocks which contain potash feldspar just as an accessory component. Used widely in recent literature, the term tonalite corresponds practically rather Lindgren's original definition. Since on the basis of plagioclase present as predominant main component the examined rock is doubtless of dioritic character, it seems to be justified to name it quartz diorite rather than granodiorite.

Chemical composition of quartz diorite:

Constituent	Weight percent
SiO_2	60.04%
TiO_2	0.80
Al_2O_3	16.91
Fe_2O_3	0.88
FeO	5.38
MnO	0.18
MgO	2.10
CaO	5.85
Na_2O	2.79
K_2O	2.34
$-H_2O$	0.15
$+H_2O$	1.32
CO_2	1.05
P_2O_5	0.10
S	0.08
	99.97%
$-O$	0.04%
	99.93%

According to *Niggli*'s classification, the rock is a Pacific magmatic product of quartz dioritic composition. Placed in *Osann*'s triangular diagram, it seems to belong unambiguously to the quartz dioritic magmatic type *(Fig. 5)*.

Niggli's parameters:

si	al	fm	c	alk	ti	p	k	mg
207.7	34.5	29.3	21.6	14.6	2.1	0.2	0.36	0.37
o	c/fm	co_2	qz					
0.08	0.74	4.99	49.49					

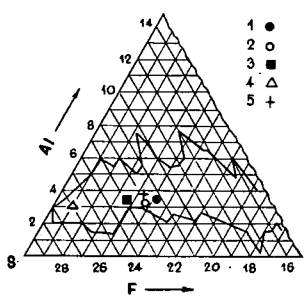

Fig. 5. Dioritic and granitic rock types plotted on the S Al F triangle diagram of *Osann*'s system. Legend: *1.* Quartz diorite, Balatonfenyves, Hungary; *2.* Quartz diorite, average value (from literatur); *3.* Granodiorite, average value (from literatur); *4.* Granite, Velence Mountain, Hungary, average value (from literatur); *5.* Granite, a type close to quartz diorite, Velence Mountain, Hungary (from literatur).

Niggli's bases:

$Q = 45.7$	$L = 41.3$	$M = 13.0$
$\pi = 0.41$	$\gamma = 0.05$	$\alpha = 4.19$

Within the earth crust magmatic products of this type occur in form of minor intrusions or as marginal zones of major intrusive masses. The structural relations of its occurrence being unknown, the direct connection of the rock to the Carboniferous granite of the Velence Mountains cannot be confirmed, even though such a connection is quite probable. As stated by GY. BUDA [1969], who investigated the Velence Mountains granite, in terms of the optic axial angle of the potash feldspar of this post-kinematic orthogranite is a monoclinic variety characterizable by a lower degree of Al/Si order, high temperature of formation, and rather rapid cooling. The crystals are either finely microperthitic or do not show any perthitic texture. With its even more advanced disordered structural state and its definitely cryptoperthitic texture, the potash feldspar of the Balatonfenyves quartz diorite may correspond to the marginal zone of the granitic mass.

The chemical and mineralogical compositions of the rock, differing from those of the Velence Mountains granite may be due to contamination of the marginal zone. In case of hybrid magmas of granodioritic — quartz dioritic composition the phenomenon of contamination is a generally accepted fact. The contaminated character of the quartz diorite of Balatonfenyves is evidenced by a peculiar mineral assemblage:

diopside (grammatite) → hornblende → biotite
ilmenite → titanite → anatase (leucoxene)

The effect of contamination can be characterized by an increase of CaO, FeO and MgO as well as by a decrease of the alkalis and SiO_2.

Chemical considerations and empirical data suggest that a rock of quartz dioritic composition can be brought about as final product in the case of a granatic melt coming into contact with a country rock of carbonate or basic composition (gabbro, — amphibolite): a process resulting in contamination. For lack of information, it is only with reservations that we can conclude as to which of the processes may have affected the rock under consideration. The presence of diopside admitted on account of grammatite, the comparatively great abundance of anortite molecules in plagioclase and the reductional character ($O_{Fe} = 0.33$) of the rock seem to favour the assumption of a contamination connected with carbonate rocks rather than with basic ones.

A comparison of the trace element data of the rock with the average trace element content of the Velence Mountains granite shows an increase of Mn, Sr, V, Zn by an order of magnitude in the Balatonfenyves quartz diorite.

Let us quote the trace element data of the quartz diorite:

Mn	1 000 ppm	Ce	20 ppm
Cu	25	Zr	120
Pb	6	Sr	230
Ga	10	Rb	52
V	60		
Ti	2 500		
Zn	< 160		
Ni	< 6		

(Results yielded by X-ray fluorescence spectrography)

Co	< 10
Sr	250
Cr	< 2.5
Ba	400
Li	100

(Results yielded by quartz-spectrography)

Analysts: P. ZENTAI and G. RISCHÁK

The present writers wish to thank DR. LIDIA VITÁLIS-ZILAHY, who was so kind to deliver them the investigated sample and to convey their gratitude to chemists DR. M. EMSZT, K. SOHA-SZALAY, G. RISCHÁK and DR. P. ZENTAI for the chemical analyses and the investigations of trace elements.

REFERENCES

BARTH, F. W. [1952]: The felspar geologic thermometers. — Norsk Geol. Tidsskrift, **42,** 2, 330—339.

BOWEN, N. L., TUTTLE, O. F. [1950]: The system of $NaAlSi_3O_8$—$KAlSi_3O_8$—H_2O. — The Journ. of Geol., **58,** 5, 589—617.

BUDA, GY. [1969]: Genesis of the granitoid rocks of the Mecsek and Velence Mountains on the basis of the investigation of the feldspars. — Bull. of the IXth Congress of the Carpato-Balcan Assoc., **1,** 131—155.

CHAISSON, U. [1950]: The optics of triclinic adularia. The Journ. of Geol., **58,** 5, 537—547.

FÖLDVÁRI—VOGL, M., BÖJTÖS—VARRÓK, K. [1968]: Vergleichende geochemische Untersuchungen an Graniten aus Ungarn. — Acta Geol. Acad. Sci. Hung. **12,** 1—4, 99—115.

LAVES, F., VISWANATHAN, K. [1967]: Relations between optic axial angle and triclinitic of potash feldspars and their significante for definition of „stable" and „unstable" statues of alkali feldspars. — Schweiz. Min. und Petr. Mitt., **47,** 1, 147—161.

MACKENZIE, W. S., SMITH, J. V. [1955]: The alkali feldspars: I. orthoclase-micropertithes. — Amer. Miner., **40,** 7—8, 707—732.

MARFUNIN, A. S. [1962]: Some petrological aspects of order-disorder in feldspars. — Miner. Mag., **33,** 298—314.

NIKITIN, W. [1936]: Die Fedorow-Methode. Berlin.

DE SÁENZ, I. M. [1967]: Alkali feldspar crystallization. — Schweiz. Min. und Petr. Mitt., **47,** 1, 87—97.

TUTTLE, O. F., KEITH, M. K. [1954]: The granite problem: evidence from the quartz and feldspar of a Tertiary granite. — Geol. Mag., **91,** 61—72.

TUTTLE, O. F. [1952]: Optical studies of alkali feldspars. — Amer. Jour. Sci., Bowen vol. II., 553.

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A STUDY OF MANGANESE ORE DEPOSITS, LAS BELA, WEST PAKISTAN

SYED IQBAL ALI

INTRODUCTION

Manganese deposits in Pakistan have been reported from Las Bela, Hazara, Kohat, Azad Kashmir and Nushki. Deposits of Las Bela and Hazara are comparatively larger than other occurrences.

In Las Bela, the manganese ore bodies chiefly consists of oxide minerals with minor quantities of silicate and carbonate minerals. They are invariably associated with greenstones and frequently with calcareous and ferruginous shales. Greenstones are characterized by the presence of plagioclase sodic felspares, chlorites, sphene and epidote. The effusive phase of the greenstones is represented by submarine pillow lavas.

Most of the important ore bodies are located at the contact of pillow lava and red shales. Manganese ore bodies are in the form of lenticular beds except for Siro and Sanjro where manganese minerals are emplaced mainly along cracks, fractures and other such structural features [MASTER, 1956, 60]. This paper includes a brief description of three typical deposits of the area (Siro, Sanjro and Khairiri). An attempt has been also made to evaluate the ores and explain the origin of the deposits.

GENERAL GEOLOGY

Reconnaissance geological mapping of the Las Bela region has been done by Hunting Corporation. The lithology and succession, known to us, is of generalized nature and requires revision and mapping on a large scale.

The part of the region covered in this study, is a complex of several rock types, including intrusives of different ages and a sequence of sedimentary rocks containing extrusive volcanics. The Pab range borders the alluvial plain of Las Bela to the east. The main feature consists of Cretaceous shales and limestones, being penetrated and intruded by rocks of intermediate to ultrabasic composition. The nature of relationship of pillow lava and shales give sufficient evidence that the extrusion of lava occurred at various intervals, thus forming a sequence of alternating layers of pillow lavas and sedimentary rocks. This alternating sequence is penetrated by sills and dykes of various composition (mainly doleritic and diabasic).

Apart from volcanics, larger concordant greenstone bodies of intrusive nature, represent a later stage of igneous activity. At their contact with shales there is no visual marked change in the mineralogy and other physical characteristics, an evidence of low temperature of the magma at the time of intrusion. At places, where intrusions are in contact with pillow lavas, xenoliths, engulfed in greenstones are observed.

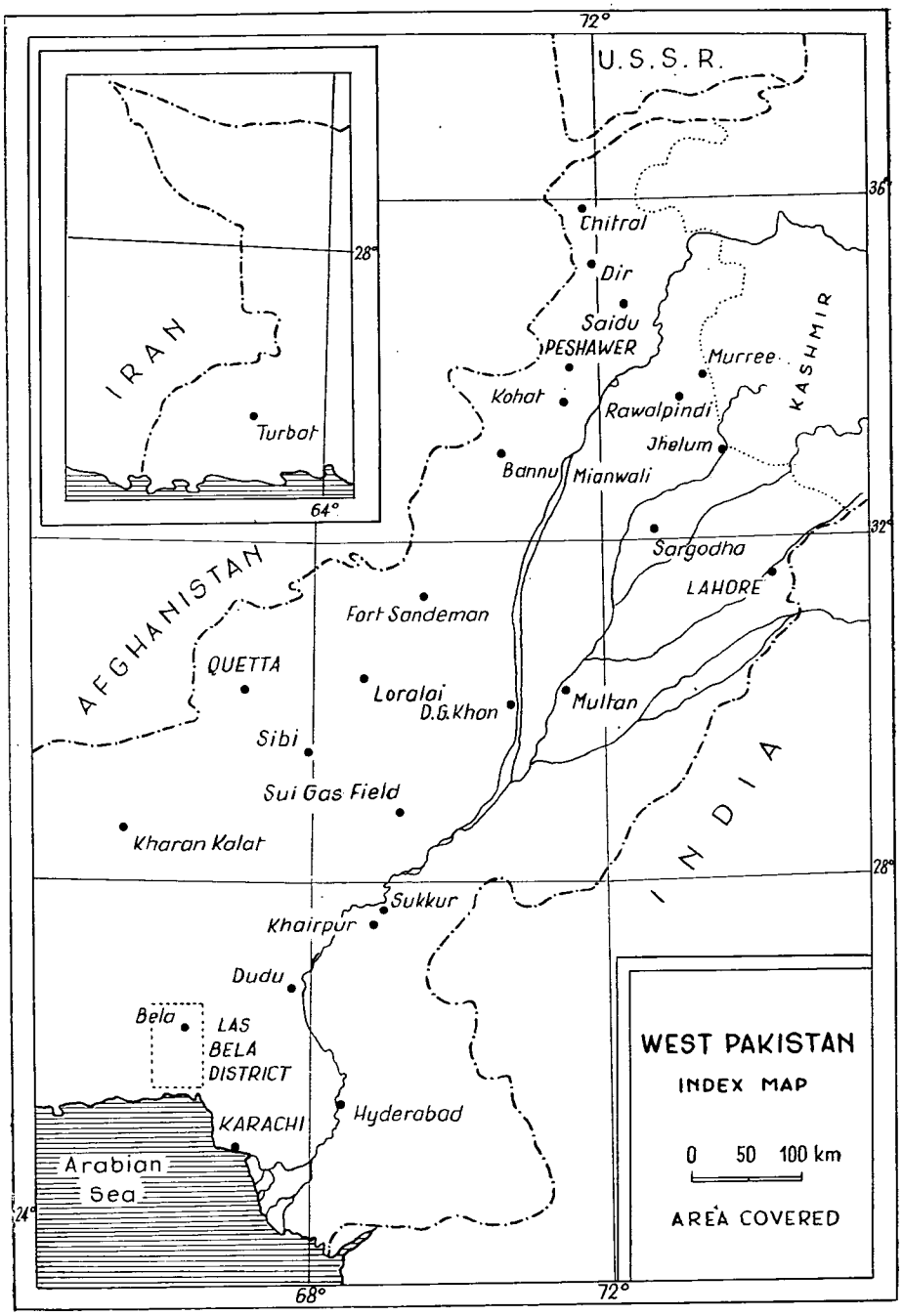
72°
U.S.S.R.
36°
Chitral
Dir
Saidu
PESHAWER
Murree
KASHMIR
Kohat
Rawalpindi
Jhelum
Bannu
Mianwali
Sargodha
LAHORE
32°
IRAN
28°
Turbat
64°
AFGHANISTAN
Fort Sandeman
QUETTA
Loralai
D.G.Khan
Multan
Sibi
Sui Gas Field
Kharan Kalat
INDIA
28°
Sukkur
Khairpur
Dudu
Bela
LAS
BELA
DISTRICT
KARACHI
Hyderabad
Arabian
Sea
24°
68°
72°
WEST PAKISTAN
INDEX MAP
0 50 100 km
AREA COVERED

Fig. 1.

The sills and dykes at various localities seems to be a surfacial representation of intrusive bodies. The paragenetic relationship of the rock types and lithological association is typical of an Euogeosyncline at an early stage of orogeny.

Generally, the ore bodies are bounded and traversed by comparatively minor faults, but they de not give evidence that the manganese mineralization is in any case related to them. Slickensides and striations with shining surfaces show that the ore bodies have suffered post depositional diastrophism.

MANGANESE DEPOSITS

In Las Bela, the manganese ore minerals bearing bodies range from mere showings to deposits containing many thousand tons of high grade manganese ore to make them worth exploitation on commercial scale. Manganese has been reported from many localities. The following localities are important from mineralogical and economic point of view.

1. Siro Dhora
2. Sanjro Dhora
3. Jabli Dhora
4. Sukkan Dhora
5. Khairiri Nai
6. Giddar Dhora

The areas of manganese mineralization at Siro and Sanjro localities are larger as compared to other deposits, mentioned above, but the average Mn content is far lower. Manganese ore bodies are located mostly at the contact of pillow lavas and the overlying red shales, except for the locality (Sukkan Dhora) where red shales are underlain by serpentinites and volcanics are absent.

Previously, Siro and Sanjro Dhora areas have been investigated by a number of geologists. VREDENBERG and TIPPER were the first to report manganese from this area in 1904—05 [1909], W. N. KHAN, S. M. N. RIZVI and S. H. A. SHAH [1951] visited the areas. MASTER [1956, 1960] for the first time mapped Siro and Sanjro deposits on a large scale . The deposits were also sampled by digging trenches and channels. A complete summary of earlier work together with the preliminary conclusions reached on the investigation carried out by the author under the guidance of PROFESSOR VALIULLAH are contained in his Presidential Address to the Earth and Physical Sciences Section of the Scientific Society of Pakistan, Karachi Meeting, 1968.

Siro Dhora

Manganese mineralization has mainly emplaced along cracks and other such features in a dolerite sill [MASTER, 1956, 1960]. The sill is traversed by faults at many places with the result that its continuation is terminated at many places. The sill is intruded at the contact shales and pillow lavas. The shales acquire red colour near their contact with igneous bodies. Overlying the shales are red to whitish grey siliceous rocks and jasperoids. The siliceous rocks also contain impregnations of manganese oxide minerals and limonite.

Previously, the area has been investigated by the Geological Survey of Pakistan and the results of the channel samples MASTER [1956, 1960] gave an average of 5% Mn. The outer zone of the spheroids of sill and along cracks, contain a high percentage of manganese as a result of surfacial weathering but the enriched zone is very

thin as compared to the area of mineralization. However, at places near the contact of sill with shale, the mineralization is comparatively richer and such zones can be traced for considerable distance. This type of enriched zones at places attain a maximum thickness of 3 feet and a length of 50 feet, and consequently grade into barren sills. The ore is hard and highly siliceous.

Chemical analysis of a chip sample shows that it contain:

SiO_2	28.66%
MnO	23.81%
MnO_2	11.14%
Fe_2O_3	12.44%
Al_2O_3	0.52%
P_2O_5	0.068%
S	0.287%
CaO	5.05%

If mining is done on a small scale, supplemented by breaking into (3×3") pieces and sorting, a considerable enriched portion of commercial grade ore can be recovered.

With the collaboration of a local Mining Company and specifications supplied by a Japanese Firm. A 100 Kilograms ore (as representative sample) by mixing in various proportions of different grade and of course keeping in view the bulk of the ore lying at the mine head. The analytical report suggests that such ores can be utilised commercially.

Mineralogical studies with the help of X-ray diffraction technique and ore-microscope reveal the presence of braunite as the major constituent of the manganese minerals, usually associated with bixbyite (sitaparite), limonite and hematite, as iron minerals. The ores of Siro and Sanjro are much higher in iron content as compared to other deposits. The high content of calcium and silica is just by the presence of calcite and various forms of silica, as gangue. Calcite is commonly found to have replaced braunite. Pyrolusite is abundant in the outer zones of spheroids.

Sanjro Dhora

Sanjro deposit is located at 24 miles north of the town Bela, exposed at three isolated hillocks. Manganese mineralization rock association and minerals assemblage is nearly the same identical as to Siro Dhora deposit, except the zone of mineralization is thicker and high in Mn content. Apart from fracture and crack fillings and local replacement: certain polished sections of the ore show crude layering of manganese minerals.

BOGUE [1962] calculated a total of 21,500 long tons of which 7,100 long tons of ore contains 20—44% Mn on conservative basis. On breaking the ore into small fragments (4×4"), grade can be improved considerably. Nearly 200 tons of sorted ore lying at the mine head, partial analysis of a grab sample showed that it contains 40% Mn and 12% SiO_2.

Khairiri

The ore body occupies a part of the terrace of Khairiri Nai (stream) and attains a height of 40 feet from the present stream bed.

Exposed at the slope of pillow lava, dipping at an angle of 18 degrees, the ore body has a lenticular form with distinct layering which pinches out in all directions.

The deposit is under and overlain by red to pinkish shales. Thickness of the deposit varies from few centimeters to 14 feet, in the centre. The exposed surface of the ore can be traced for 400 feet along dip slope, while the width varies from 50 to 100 feet. Field observations indicate that prior to the uplift of the area and subsequent deepening of the stream channel, nearly the lower half portion of the deposit was drowned below the groundwater level.

Water table seems to have played an important role in determining the mineralogy of the lower half portion of the deposit. On the basis of physical characteristics of the ores, the deposit can roughly be divided into two parts.

1. The upper part, which consists of hard, massive and cavernous or spongy ores.

2. The lower part, substantially consists of soft and powdery ore. This abrupt change in the appearance of ores is an striking feature of the deposits. There are local evidence to favour the idea that a part of the ore body has remained below the water table (formed by stream). The presence of stream bed sediments, silt and gravel covering the lower half of the deposit.

At the top end, the ore bed contains two thin lenses of chert and the contact between chert and ore bed is sharp.

Microscopic studies reveal that hard and massive ores, commonly exhibit colloidal banding, pisolites, concretions and other such features. The soft and powdery ores are dominantly composed of minute concretions, open space fillings with unoriented needle-like crystals of pyrolusite and alteration of primary minerals.

The deposit is separated by a thin bed of red shale containing abundant pods of manganese (mostly braunite). The thickness of the shale bed gradually increases downdip and with that the ore bed thins out. Replacement on a minor scale along the partings of red shales indicate that manganese bearing solutions have trickled downed along such partings. Other field evidences also indicate the outlet of hot solutions was very close to the proximity of the deposit. X-ray diffraction patterns prove that braunite is the major constituent, followed by pyrolusite, manganite, in order of abundance. Manganoan calcite is found in small veins usually accompanied by silica. Rhodochrosite was found only in one sample. Calcite and various forms of silica are common gangue minerals.

The distribution of manganese in the deposit is not uniform. However, a number of samples showed that the lower part of the bed is more siliceous and lower in manganese content than the upper manganese layer, overlying the thin bed of red shales. On the basis of numerous analysed samples representing different parts of ore bodies, sorted and low grade ores, it may be safely assumed that 7000 tons of high grade ore can be mined. Fifteen hundred tons of high grade ore has already been shipped to Japan from this mine.

MINERALOGY

Mineralogy was studied with the help of petrographic microscope, ore microscope and X-ray diffraction technique.

Polished and thin sections of ore samples were prepared. Micro samples of the minerals were scooped from the polished sections, using a diamond pointer under the microscope. Although, it was not always possible to obtain a pure mineral powder. The powder was mounted on a fine glass fibre. A number of samples were also tried with diamond-gelatine technique. Fe radiations (1.9373) were employed through-

out with Mn filter. Most of the patterns were taken on 11.7 cm. camera and few with 5.96 cm camera.

The manganese minerals can be grouped into:

1. Oxides *2.* Silicates *3.* Carbonates

Manganese oxide minerals are the most abundant and form bulk of the ore bodies. The silicate minerals are usually associated with oxides but in minor quantities. Carbonate minerals are scarce, represented by manganoan calcite and rhodochrosite was recognized only in one sample.

Oxides

Among oxides, braunite is the most abundant, followed by pyrolusite, manganite, bixbyite and hollandite in order of abundance.

Braunite

Braunite constitutes the major portion to the ore, it can usually be found, where the ore body is hard, without the effects of superficial weathering. A reddish brown silicate is commonly associated with it. It forms colloform banding, concretions, pisolites, pellets and pods of various dimensions. Braunite is associated with bixbyite at Siro and Sanjro Dhora. — Pyrolusite is the common alteration product of braunite.

Pyrolusite

Pyrolusite is generally considered as a '*supergene mineral*', and on the basis of textural relationship and the predominence of pyrolusite in the zone exposed to weathering below the 'drowned water table' and in cracks, provide sufficient evidence that pyrolusite is mostly supergene. Pyrolusite specimen are very soft and difficult to prepare a polished section. The pyrolusite section, thus prepared, consist of small pellets with contrasting concentrical bands of pyrolusite. Such specimens are intensively traversed by veinlets of calcite. Cracks are, generally, filled with unoriented needle-like crystals of pyrolusite and this texture suggest an open space filling.

Manganite

Manganite was indentified is ore specimen from Kairiri and Sukkan Dhoras in two specimens is found to be associated with hollandite and in some sections with reddish brown silicate. It exhibits a faint stratification in a number of samples. Hollandite associated with manganite seems to be primary or hypogene. It is very rare to find hollandite associated with manganite (D. F. HEWETT, personal communications). Bixbyite is also a primary mineral and shows a common association with braunite.

ORIGIN

The source and environments of deposition of the manganese deposits, whether considered as proper sedimentary or hydrothermal have been debated for the last 100 years. Extensive research is being done all over the world to determine the mode of origin and more exact knowledge is required for exploring new deposits of manganese in future. The complexity is created by the varying nature of manganese deposits all over the world.

However, volcanism as a possible source of manganese, for the deposits associated with volcanics, such deposits are frequently characterized by their bedded nature,

in the form of lenses or similar features. The idea was first seriously put forward by French geologists working in Morocco (1934), described some of the occurrences of manganese as '*Volcanogenic-Sedimentaire*'. Later this was applied by Germans as '*Exhalative-Sedimentaire*'. It is believed that hot solutions connected with volcanism, enriched in Mn, Si, Fe and certain trace elements on combining with sea water are oxidized and precipitated as sediments.

The manganese deposits of Las Bela range from hydrothermal to volcanogenic-sedimentary in origin. The source of manganese in either case was volcanism. Following volcanism, hot solutions carrying Mn mixed up with marine waters, MnO was oxidized by oxygen to higher states of oxidation and precipitated, whereas, at Siro Dhora and Sanjro Dhora took place mineralization mainly along fractured zones (hydrothermal). The above statement is based upon wast field observations, mineral assemblage, and chemical composition of the ores and minerals. The main features that brought us to this conclusion are:

1. Bedded nature of the deposits.
2. Sharp contact of the ore bodies and the enclosing rocks.
3. Most of the polished sections show, faintly stratified manganese oxide minerals or textures typical of precipitation from gel state (colloform banding, concretions etc.) and on these grounds it can be conveniently argued that deposition of manganese took place under quiet water conditions.
4. Absence of large discordant relationship of ores and the host rocks.
5. The most important evidence to support the relationship of Mn carrying solutions and pillow lavas, is the presence of numerous small veinlets of manganese that cut across the pillows underlying the deposits. The spheroids of lavas are stained with films of manganese along joints and fractures.

A number of samples were sent to D. F. HEWETT, for his expert opinion. His interpretations suggest that the persistent traces of layering in manganese oxide minerals lead to confirm the idea of deposition of manganese oxide minerals under quiet water (marine) conditions, following the extrusion of lavas.

It seems that the ores are not related to any particular period of eruption, but many, at intervals. True to the extent that such deposits show abnormal concentration of certain trace elements (W, Th, Ge, Pb, Cu, Zn, etc.) [HEWETT, 1966, STRAKHOV, 1968], as mentioned earlier. A number of samples were analysed with X-ray fluorescence and spectrographic methods.

The usual association of quartz, chert, calcite, manganoan calcite, barite and copper minerals identified in one locality, bring us further evidence.

It is also believed that the hydrotherms located at various centres near ore-deposits were fluctuating in their chemical composition.

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REFERENCES

AGUIRRE, LUIS and MEHECH, SONIA [1964]: Stratigraphy and mineralogy of the manganese sedimentary deposits of Coquimbo Province, Chile. — Econ. Geol., **59**, p. 428—442.

BOGUE, R. G. [1963]: Manganese deposits at Sanjro near Bela, Kalat Division, West Pakistan. — Min. Inf. Circ., Geol. Surv. Pakistan, No 9, 16pp.

FLEISCHER, M. and RICHMOND, W. E. [1943]: The Manganese Minerals: A preliminary report. — Econ. Geol., **38**, p. 269—286.

HERON, A. M. [1954]: Directory of economic minerals of Pakistan. — Geol. Surv. Pakistan Recs., **VII**, Pt. 2.

HEWETT, D. F. and FLEISCHER, MICHEL]1960]: Deposits of manganese oxides — Econ. Geol., **55**, p. 1—55.

HEWETT, D. F., FLEISCHER, MICHAEL and and CONKLIN, N. M. [1963]: Deposits of the manganese oxides — supplement. — Econ. Geol., **58**, p. 1—55.

HEWETT, D. F. [1966]: Stratified deposits of the oxides and carbonates of manganese. — Econ. Geol., **61**, No. 3, pp. 431—461.

HUNT, C. B., MCKELVEY, V. E., WIESE, J. H. [1942]: The Three Kinds manganese district, Clerk Country, Nevada. — U. S. Geol. Survey Bull., **936—L**, p. 297—319.

HUNTING SURVEY CORPORATION LTD. [1960]: Reconnaissance Geology of part of West Pakistan, Maracle Press Limited, Ottawa, Canada, pp. 550.

KRAUSKOPF, K. B. [1957]: Separation of Iron from Manganese in the Formations of Manganese Deposits in Volcanic Association. — 20th. Internat. Geol. Cong., Manganese Symposium **1**, p. 119—131.

MASTER, J. M. [1960]: Manganese showings of Las Bela District, West Pakistan, No. 13, pp. 18.

PARKS, C. F., JR. [1956]: On the origin of manganese. — 20th Internat. Geol. Cong., Mexico City, Symposium Manganese **1**, p. 75—98.

PARK, C. F., JR. and COX, M. W. [1944]: Manganese deposits in the Sierra Maestra, Cuba. — U. S. Geol. Surv. Bull., **935—F**, p. 307—355.

RAMDOHR, P. [1956]: Manganese Ores. — 20th. Internat. Geol. Cong., Mexico City, Symposium Manganese.

SHATSKIY, N. S. [1964]: On manganiferous formations and the metallogeny of manganese, Paper-1, Volcanic-sedimentary manganese formations. — International Geology Review **6**, p. 1030—1056.

STRAKHOV, N. M. [1968]: Geochemistry of a sedimentary manganese ore-forming process. — Academy of Sciences of the USSR, Geological Institute, Moscow.

VALIULLAH, M. [1968]: Manganese deposits of Las Bela State. — All Pakistan Scientific Society Conference, Karachi (Presidential Address).

VARENSTOV, I. M. [1964]: Sedimentary manganese ores. — Amsterdam, Elsevier Publishing Co., 119 p.

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THE INSTRUMENTAL ANALYSIS OF MODERN VERTEBRATE TOOTH AS FOSSIL MODEL MATERIAL

GY. SZÖŐR

INTRODUCTION

The detailed biochemical instrumental analytical investigation of the Mollusca shell, as well as a similar interpretation of the taxonomic and fossilization problems directed attention to the thermoanalytical research of the biogenic calcified systems.

In recent years [SZÖŐR, 1969] in the course of the complex thermoanalytical investigations of the modern and fossil Mollusca shell by means of the Derivatograph apparatus [PAULIK *et al.*, 1958] — as "$CaCO_3$-konchiolin" inorganic-organic system — it was verified that a new investigational direction was devised which reflected taxon specificity and followed the line of fossilization processes.

In the course of the investigations it became obvious that the inorganic structure variations brought about by the specific protein, the quantity and ratio of the inorganic and organic components, manifest themselves perceptively, thereby determining the thermoanalytical processes. Thus, the DTA-, DTG-, and TG-relations, in conformity with modern species, reflect species-specific information, or, in the case of Pleistocene, Pliocene, and Tortonian fossils under favourable embedding conditions, reflect signals interpreting genetic specificity. The reproducible results obtained from the fossiliferous species ensured an identification possibility of the hardly evaluable fragmental material obtained from the sediment. The work of comparison took into account the diverse palaeocologic and fossilizational possibilities. Such a comparison of the samples of the diverse fossiliferous biotopes (facies) [SZÖŐR, 1970, 1971] offered new facies-indication possibilities of relying on absolute index numbers. The elaboration of this new research direction is still in progress, but we deemed it absolutely necessary to extend the investigations from the Mollusca group to the Vertebrate taxon. This endeavour was stimulated by our desire to get acquainted with the thermoanalytical properties of the "apatite-collagen" inorganic-organic biogen system. Furthermore, to establish whether we can obtain information about the modern Vertebrate species with the method elaborated in connection with the Mollusca shell, or by any other comparative systematic method, or — in the case of fossiliferous species — paleosystematic, facies-indicational information characteristic of fossilization. The results reported in this paper give an account of the experiences gained while elaborating the course of methodology to be followed in a series of experiments which will probably take a long time.

The vertebrate fossil material obtained in masses from the sedimentary rocks contains for the most part bones and teeth, only rarely do other components come to light, *i. e.* primarily scales of fishes, hides, hair formation, and it would certainly create a sensation to find again the carcass of a mammoth frozen in the ice, or a fossil either mummified or embedded in bitumen or fossil wax. The biochemical evaluation is of course confined to these "ideally" fossilized findings. KERNBACH [1924], BOYD et BOYD [1934, 1937], YAMADA [1934], GRAF [1949], as precursors determined albumins, the ABO blood group, and active lipase and histamine from human mummy material. STEPPUHN and LJUBOWCOWA [1930] made us acquainted with the active proteolitic enzyme of a mummy and mammoth. THIEME *et al.*, [1956] determined a blood group from a fragment of a human pleistocene skull. SINEX et FARIS [1959] examined the gelatine of the antlers of a 12000 year old stag, DROZDOWA [1962] the collagen of the scalp of a mummified amphibian from the Lower Permian. HELLER [1966] revealed the fossilizational differences of the diversified vertebrate material obtained from the Anisian and Ladinian bitumen shale, the Liasic Posidonomia shale, and from the Rancho La Brea asphalt pit, thereby verifying the preserving effect of the bitumen embedding. WYCOFF [1969] reported on the spectrum of protein amino acids isolated from the Dinosaurus bones of the Jurassic and Cretaceous period.

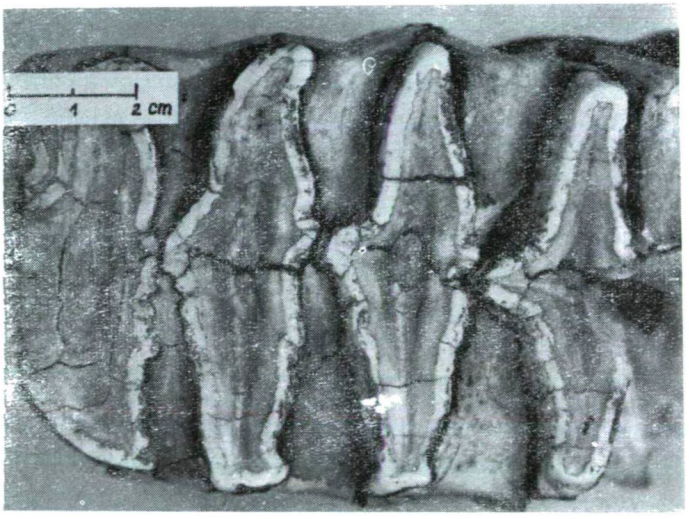

Fig. 1. Structures of the Loxodonta africana tooth. Top view, cement without, enamel in the middle, dentine within.

We attribute great importance to these results. On the one hand they prove that also the vertebrate remains have their specific proteinmaterial survival possibility, and that the subsisting organic material as indicator shows that the inorganic structures have not yet crystallized, have not yet been dissolved, but still preserve their original pattern. On the other hand they indirectly call attention to the fact that it is

worth while to go on investigating systematically the less "ideally" subsisting tooth and bone remains with similar or other methods. In general we chose the tooth material as object of our investigations, justifying our decision with the following reasons:

1) The great number of fossil teeth is, generally better preserved than the bone material, in the case of modern research material: a better "access" possibility.

2) The tooth reflects the evolutional, phylogenetic changes much more sensitively than the bone material, in this respect it is a morphologically well defined investigation material, and suitable for comparison.

3) The study of the taxonspecific, diversified structure assemblage brought about by the collagen of the tooth, a typical inorganic substance-building protein, has for a long time been an effective method for systematic problems [CHALINE, 1968].

4) The thermoanalytical research of the tooth as human material has already begun in our country [SIMON *et al.*, 1969. BERÉNYI *et al.*, 1970].

5) The crystallo-chemical aspects of the mineral components of the teeth (problem of dahllite and francolite) were investigated and analysed in detail a. o. MCCONELL [1938, 1952a, 1952b, 1960].

The present investigations were carried out on the lamellar molar of a recent African elephant (Loxodonta africana) obtained from the material of the museum of the Hungarian Geological Survey *(Fig. 1)*. The selection of the sample was justified by the following points of view: The objective of this work was to get to know which of the instrumental analytical methods employed by us would be the most suitable for revealing the physico-chemical differences of the structure units constructing the tooth. The available possibilities must be considered, and we must select the method or methods which seem to be the most appropriate, by means of which we at first compare modern species with one another, and then the tooth material of corresponding fossils. Since it is a question of elaborating several procedures, we needed a great deal of dentin, enamel, and cement which could be separated analytically. By means of its size and morphological structure the Loxodonta tooth meets these requirement in every respect. The selection was further justified by the fact that the Loxodonta tooth differs from the structure of many vertebrate taxon teeth by a structural unit, the presence of the cement layer. The chemical, physical investigation and evaluation of the cement layer, to the best of our knowledge, has not been performed as yet.

METHODS AND RESULTS

Preparation

The cement, enamel, and dentin layers were separated from each other mechanically. The larger pieces were prepared with a chisel and hammer, while the enamel was cut off the dentin with a dental diamond-disc under constant cooling. The thus obtained pieces were broken up and then ground in an agate grinding-mill (heating 1 h/1°C)below the grain-domain of 0,06 mm∅. The preparations were then stored in an air-tight glass vessel. An average of the material was taken for each examination.

Though my aim was the uniform investigation of the organic and inorganic totality, yet, for the sake of evaluation, I solved the separation of the organic assemblage (protein, lipid, mucoprotein, etc.) from the inorganic fraction (carbonate-oxyapatite) so that neither should be impaired. The organic fraction was prepared in the following way: the inorganic totality, dialysed in sterile environment, was carried

into solution (0,268 M (10%) EDTA; pH 7,4) at 5°C. The organic material remaining in the dialysis-membrane was collected and lyophilized and immediately utilized after treatment (IR-spectroscopy). The inorganic fraction was obtained by dissolving the organic material by constant strirring in a solution consisting of 0,5 *N* NaOH (carbonate-free) and glycerine over a water-bath, decanting the supernatant several times, washing it with distilled water, and drying it at room temperature (Derivatography).

Microscopic comparison

A thin section was prepared from the tooth at a depth of 1 cm from the surface, parallel to the axis of the tooth, and crossing the cement, enamel, and dentin layers obliquely. The structures were examined in two different ways. With the thin section

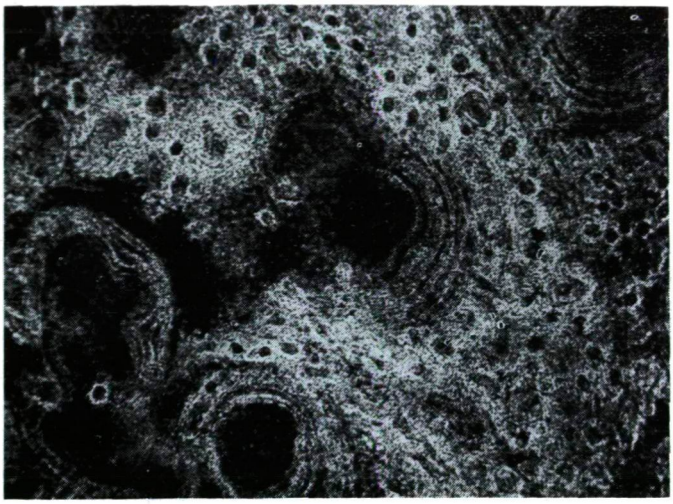

Fig. 2. A microscopic picture of cement in transmitted light, parallel nicols. Magn. 28:1.

method, in unpolarized light, the following phenomena can be observed: the cement layer is crystal-aggregated, and composed of smaller and larger spherolites, the enamel is cracked at the edges, the dentin shows a homogeneous structure *(Figs. 2, 3, 4)*. The enamel and dentin can hardly be distinguished by means of such examination.

With the replica-impression method [LOVAS, 1960] the surfaces were corroded with *N* HCl for an identical length of time, after which a replica was made with collodion. The differences between the three structural units appears very markedly when examined by means of a D-3 condensor. (Figs. 5-6-7). The sphaerolites of the cement layer show up much more plastically, the surface of the enamel is built up of hexagonal facettes, and longitudinal rib-like reliefs can be seen on the surface of the dentine layer.

Comparison with IR-spectrum

The IR-spectrum of the cement, enamel and dentine containing the original organic and inorganic fraction was taken with a UR-10 (Zeiss) apparatus in the 400—4000 cm^{-1} wave-number interval. The material was placed in a KBr -disc

(Fig. 8.). The spectra were compared with the IR-spectra taken by MOENKE [1962] under almost identical conditions. The spectra especially resemble the IR-spectra of the apatite, phosphorite samples of above author. According to these, in general the 400—1100 cm^{-1} band system denotes the bands of apatite, in the 1100—1700 cm^{-1} interval we can find the oscillations (1640 cm^{-1}) belonging to the carbonate and organic substances, in the 1700—4000 cm^{-1} interval can be seen the bands of OH and H_2O, possibly that of the NH_4^+ salts bound to the organic and inorganic structures

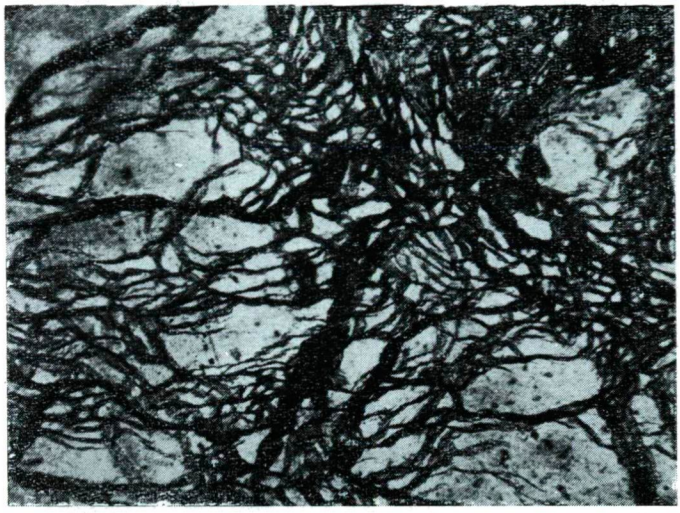

Fig. 3. A microscopic picture of enamel, in transmitted light, parallel nicols. Magn. 28:1.

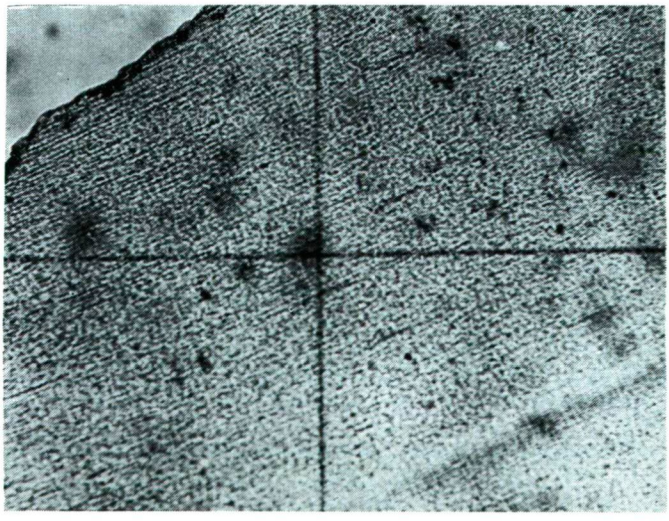

Fig. 4. A microscopic picture of dentine, in transmitted light, parallel nicols. Magn. 28:1.

with variable intensity. (It can be assumed that at 1600—1670 cm^{-1} AMID I; at 1500—1550 cm^{-1} AMID II; at 1230 cm^{-1} AMID III; at 660 cm^{-1} AMID IV; at 1410, 2420 and 2850 cm^{-1} CH_2—CO—NH bindings are seen to appear.)

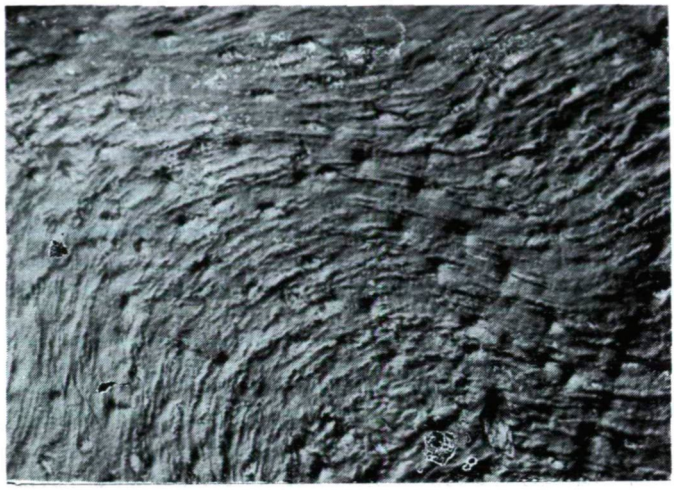

Fig. 5. The replica-impression picture of cement with a D-3 condensor. Magn. 310:1.

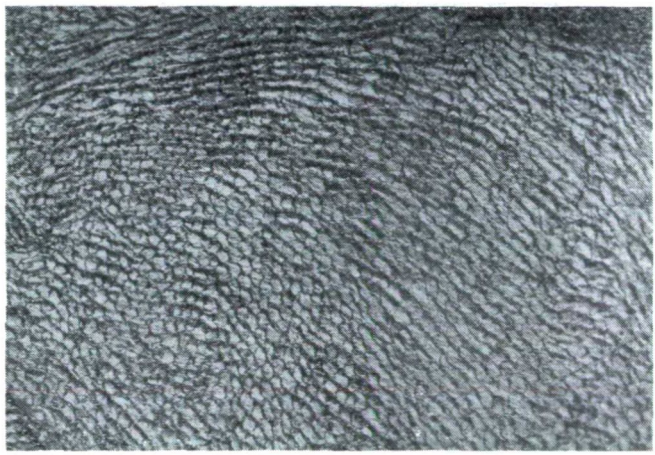

Fig. 6. The replica-impression picture of enamel with a D-3 condensor. Magn. 310:1.

When comparing the three spectra with one another, the similarity of the cement and dentin is found to be striking (more OH, organic material, carbonate), as well as their difference from the enamel.

The IR-spectrum of the organic fraction liberated from the inorganic material with EDTA was taken with a Unicam-SP 200 G apparatus in the 650—4000 cm^{-1} wave-number interval with the material in a KBr-disc *(Fig. 9)*. Though we did not touch upon the detailed evaluation of the spectra, the difference of the organic frac-

tion of the enamel layer from that of the cement and dentin layers is marked (730, 1550, 1735, 2360, 2950 cm^{-1} bands). The similarities and differences are also perceptible when the bands are compared quantitatively.

Comparison by means of thermoanalysis

The investigations were carried out with a Derivatograph apparatus of domestic made, with which the DTA-, DTG-, TG-relations were jointly analysed.

First the natural material was investigated. The cement, enamel and dentin layers were compared in the No. 2 platinum crucible under identical experimental conditions. On the basis of previous experiments the following programme was elaborated: Measurements: between 1,3—1,4 g. The volume of the inert material Al_2O_3 corresponded to the volume of the investigated sample.

The sensitivity of DTA, DTG was 1/10, the TG sensitivity was 500 mg. The motor and disc rate was 200, initial voltage 95 V, the situation of the nails: 3 rows of nails in a large disc. The samples were examined in furnace No. 1 under a quartz cup, without suction, in air atmosphere, in an interval of 20°C—1000°C. The derivatograms were evaluated on photo paper, then remodelled onto a scale of equal temperature, taking into consideration the intensity of the DTA—,DTG -curve *(Figs. 10 – 11 – 12)*.

Comparing the relations of the dentin DTA, DTG, TG *(Fig. 10)* with the data obtained during the investigations carried out on human dentin by BERÉNYI *et al.* [1970], a striking difference can be observed. The thermoanalytical processes taking place during heating can be interpreted as follows: The adsorptive and weakly bound

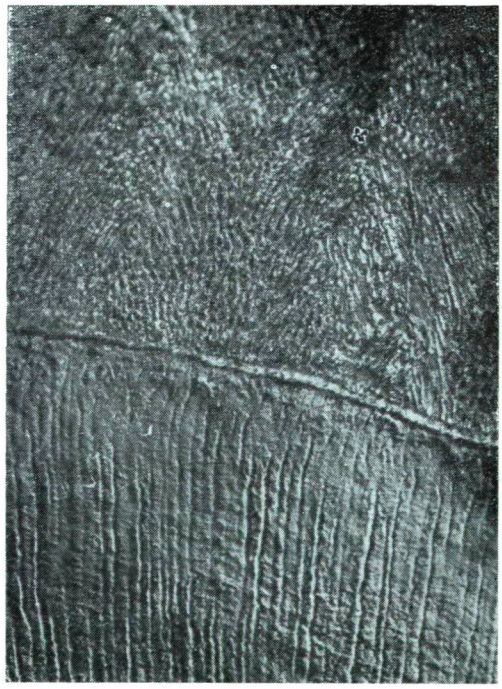

Fig. 7. The replica-impression picture of enamel (upper part) and dentine with a D-3 condensor.

water is eliminated with maximum rate from 178° C to 250° C. The beginning of the decomposition of the organic material of the tooth is closely correlated with this process. This decomposition can be compared to „cracking". The liberation of the water bound to the organic macromolecules, the initial decomposition and transformation of the organic structure, the desamination and decarboxylization of the amino acids takes place here. The process is composed of exothermic and endothermic reactions (404° exothermic and 471° C DTA-curve endothermic bend). The changes observable from 620° C on are also complex, the burning of the remaining

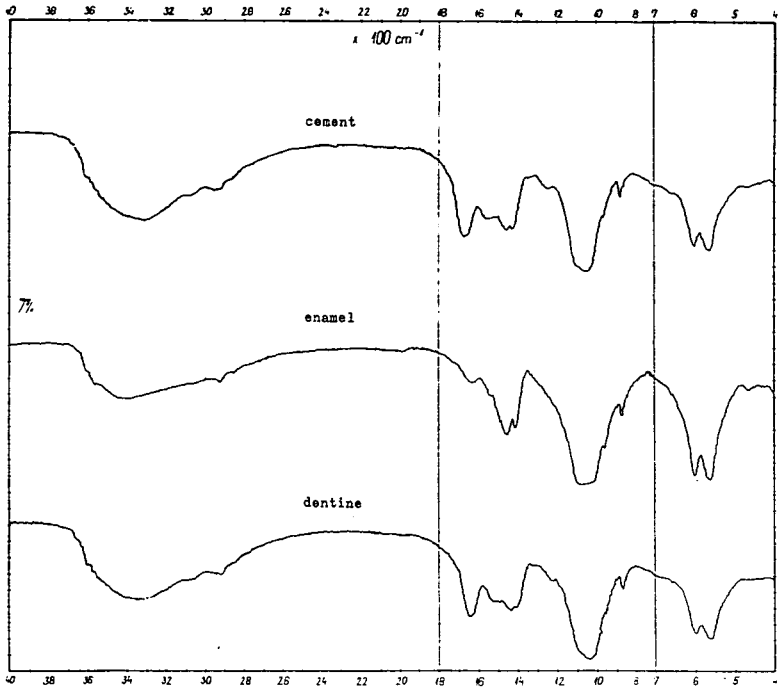

Fig. 8. The IR-spectrum of the structural components of an African elephant's tooth (charasteristic bands).

Cement cm^{-1}	Enamel cm^{-1}	Dentine cm^{-1}
	467	470
470	565	560
565	603	600
605	663	662
875	870	870
965	880	955
1050	960	1040
1240	1060	1230
1340	1415	1330
1420	1460	1410
1455	1540	1440
1668	1640	1640
2930	2850	2930
3080	2920	3070
3330	3400	3300

organic material (900° C DTA-curve maximum) predominates and covers the release of the CO_2 originating from the carbonate-apatite. In this respect we have distinguished three forms capable of liberating material.

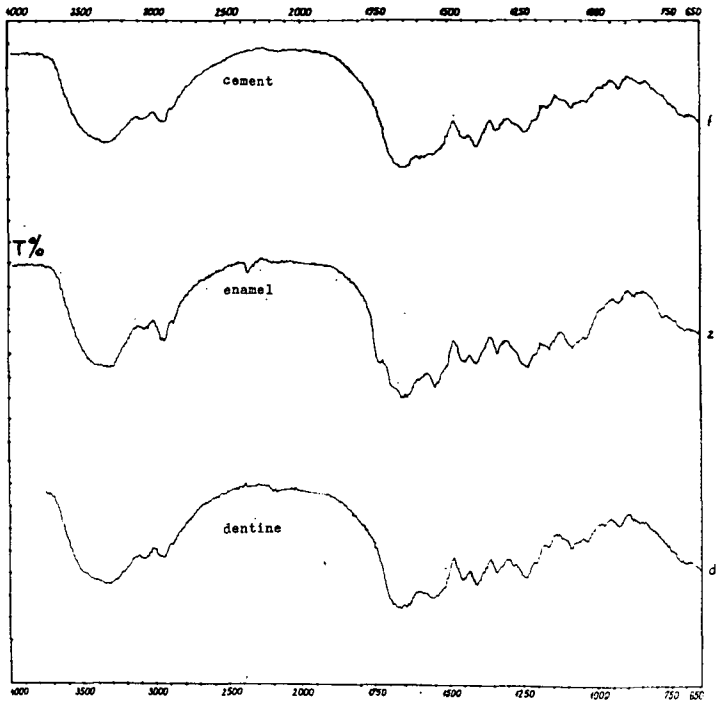

Fig. 9. The IR-spectrum of the organic fraction of pan African elephant's tooth isolated from it structural components

Cement	Enamel	Dentine
cm^{-1}	cm^{-1}	cm^{-1}
700	705	700
850	730	850
920	870	925
975	930	975
1030	1040	1030
1085	1080	1085
1168	1160	1165
1240	(1205)	1205
1335	1235	1240
1405	1335	1280
1442	1410	1335
(1550)	1450	1405
1650	1550	1450
(2160)	1650	1550
2875	1735	1660
2930	2360	2160
3080	2875	2875
3340	2930	2930
	2950	3080
	3075	3340
	3300	

The derivatogram of cement *(Fig. 11)* supplies us with an account of thermoanalytical properties similar to those of dentin. A more essential difference can be observed only among some of the TG-curve substance-liberating values, or in the decomposition taking place in the 600° C—1000° C temperature interval. The burning of the remaining organic material (DTA-curve, 917° C exothermic maximum) is more intensive, and the endothermic curves referring to the carbonate-oxy-apatite

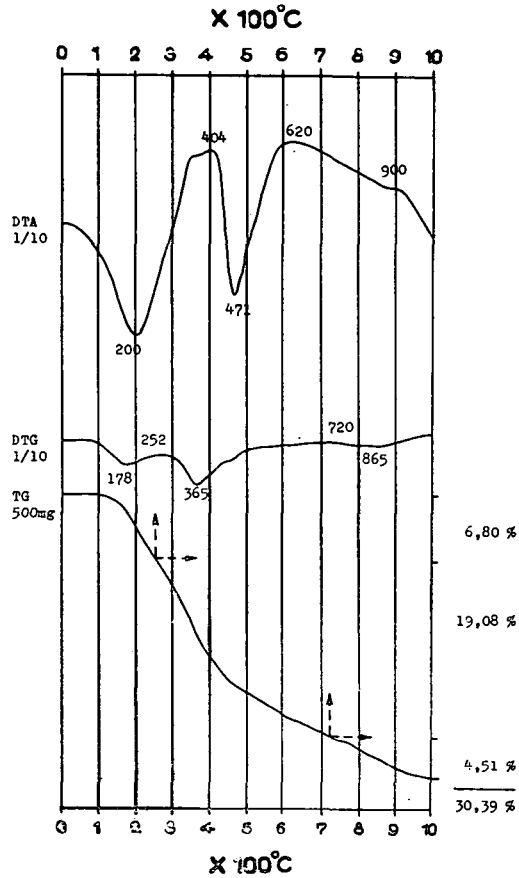

Fig. 10. The derivatogram of dentine in a platinum crucible.

also appear (DTA-curve 706° C, 842° C endothermal minimum). The thermogram differs sharply from the thermoanalytic data of human dental calculi of SIMON *et al.* [1969].

The enamel derivatogram *(Fig. 12)* differs totally from the derivatogram of cement and dentin. The essential difference can be observed in the relatively small amount of substance-liberation readable on the TG-curve. The difference can be explained by the fact that there is no endothermic process in the vicinity of 500° C.

In this case also the burning of the remaining organic material covers the endothermal processes marked by the decomposition of the carbonate-oxyapatite.

Comparing the thermoanalytical data of the Loxodonta enamel with the data of human enamel reported by BERÉNYI *et al.* [1969], the thermoanalytical processes may be said to be almost identical, the difference ensuing from the selection of the diverse DTA, DTG and TG sensitivities.

In the course of the experiments it was suggested that we must not count burning, but on slow "crack" processes in the platinum crucible in relatively oxygen-poor environment in the interval of low temperature. This decomposing process is catalytically influenced by the platinum crucible. To verify this, the heating of the samples was carried out in a ceramic crucible. LIPTAY et al. [1968] call attention to the catalytic effect of the platinum crucible and its elimination.

The thermoanalysis was performed in the ceramic crucible under experimental conditions identical to those of the platinum crucible. The converted and evaluated derivatograms are shown in *Figs. 13, 14* and *15*. A survey of the figures proves that our supposition was correct. In the case of the dentin and cement the DTA-curve

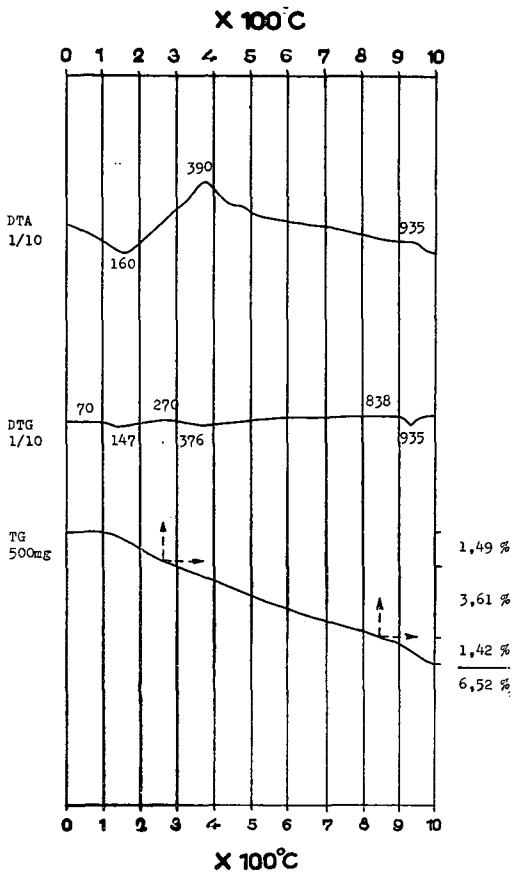

Fig. 11. The derivatogram of enamel in a platinum crucible.

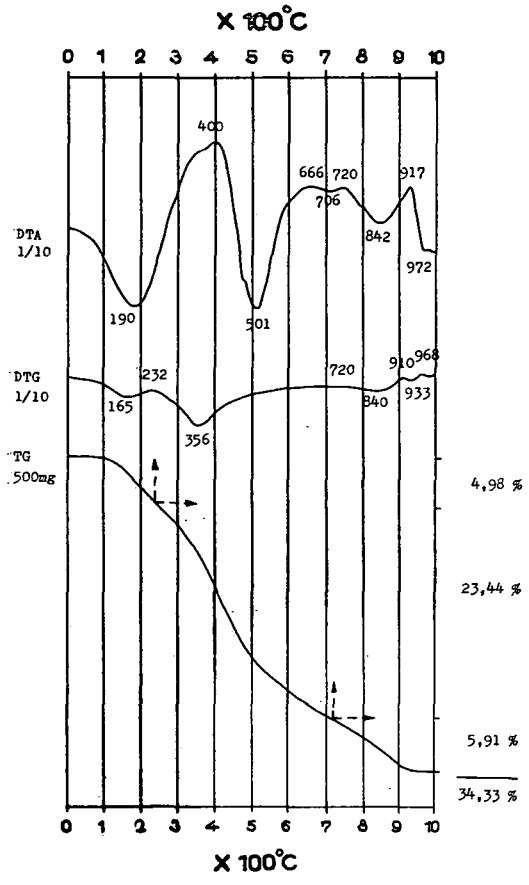

Fig. 12. The derivatogram of cement in a platinum crucible.

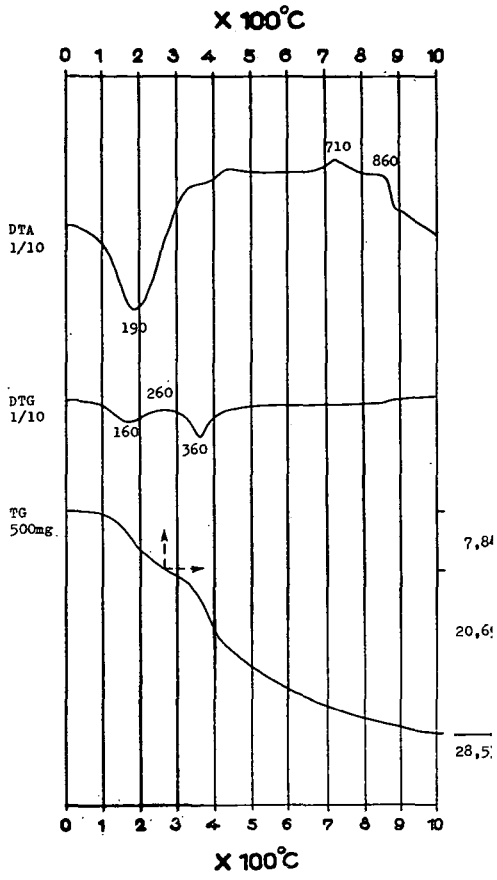

Fig. 13. The derivatogram of dentine in a cerar crucible.

changes denoting the exothermal and endothermal reactions appearing in the "crack--interval" had disappeared (or hardly appeared in the case of the cement) and the decomposition process of the organic material had shifted in the direction of the interval of higher temperature. (In dentin it takes place between 701° and 860° C, in cement at 865° C.) With this method the derivatogram of cement and dentine differs much more sharply from each other than in the platinum crucible. In the case of enamel, of course, these processes cannot be observed, since the separation of the endothermal and exothermal processes does not manifest itself in a platinum crucible, either. This fact can be explained by the small amount of the organic material. In a ceramic crucible, employing 200 mg TG sensitivity, the thermo-reactions separate much better in the interval of higher temperature.

We were not able to obtain satisfactory information about the nature of the inorganic material constructing some of the structural components when we carried out the investigations either in a platinum or in a ceramic crucible. Since we could not afford to use inert atmosphere (N_2 inert gases), we removed the organic fraction in NaOH + glycerine and examined the remaining inorganic material by employing a more sensitive programming. The investigations were carried out in a platinum crucible with 1/5 DTA, DTG sensitivity, 100 mg TG-sensitivity. The thus gbtained evaluated derivatograms are shown in *Figs. 16, 17, 18.* A survey of the fioures shows us that the exclusion of the confusing role of the organic material

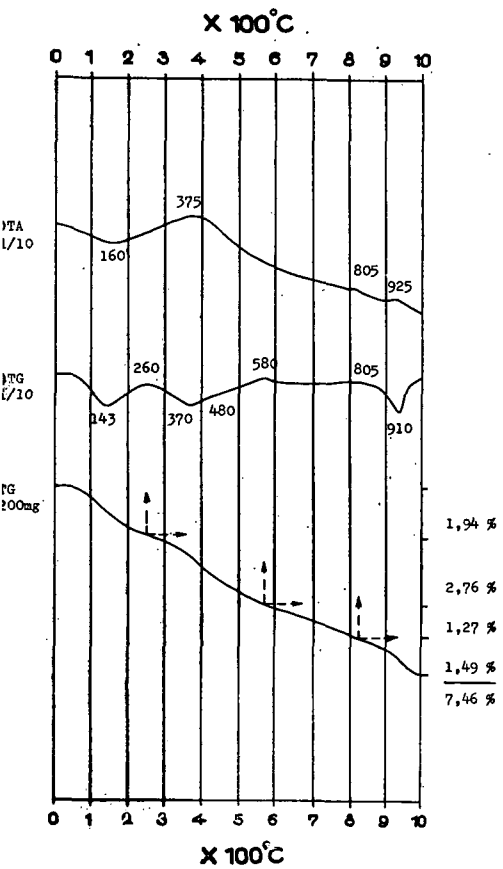

Fig. 14. The derivatogram of enamel in a ceramic crucible.

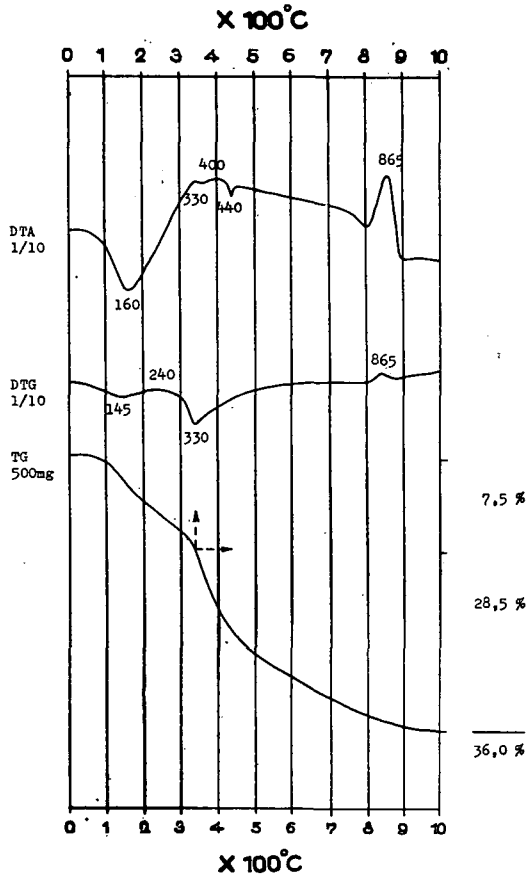

Fig. 15. The derivatogram of cement in a ceramic crucible.

was successful, though it can be assumed that some remainder of the organic material may still be enclosed by the organic structure. This organic material becomes partially hydrolysed and broken up into fragments. The thermoanalytical decomposition takes place as follows:

The adsorptive water evacuates by 240° C in the case of cement and dentin, in the case of enamel by 300° C. The OH^- bound to the inorganic structures detaches itself continuously simultaneously with the liberation of the OH^- bound to the remaining organic material as well as with the decarboxylization and desamination. This process can be followed in three steps in the case of the dentin, in the case of the cement in two steps, and in one step in the case of the enamel up to 700° C.

The decomposition of the carbonate-apatite structure begins at 700° C. The release of the CO_3^{--} takes place in two sharply separated steps. The CO_3^{--}, is bound taking into consideration the results of POSNER and DUYCKAERTS [1954] by Ca^{++} and Mg^{++}. It may be assumed that calcite and magnesite or even dolo-

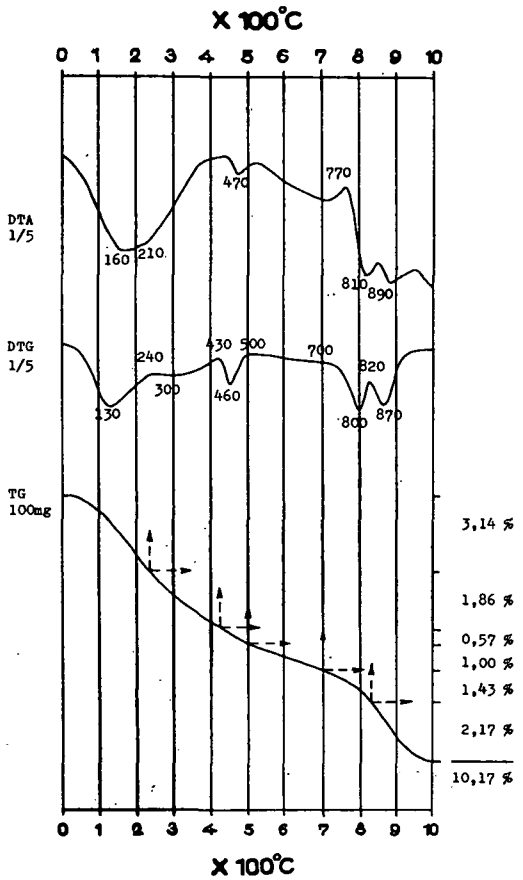

Fig. 16. The derivatogram of dentine, previously treated with NaOH-glycerine solution, in a platinum crucible.

mite are present in free state. It is to be noted that on the basis of the DTA investigations of SILVERMANN *et al*, there is no change in the thermoanalytical curve of dahllite, though, in the vicinity of 800° C, it releases some water enclosed in the apatite structure.

It is noteworthy that SCHRÄMLI and BECKER [1960] experienced and endothermal change in the course of their fluorapatite DTA investigations at 870° C.

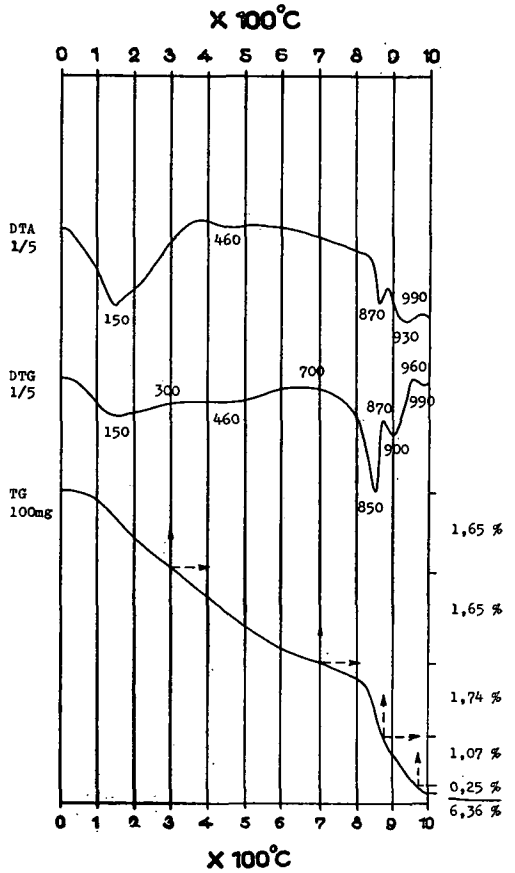

Fig. 17. The derivatogram of enamel, previously treated with NaOH-glycerine, in a platinum crucible.

As regard the enamel, a third small quantity of exothermal release of material can be observed from 960° C on, and in the case of the dentin and cement an exothermal process can be experienced simultaneously with the initial release of CO_2 (760° C, 770° C on the DTA curve). Exothermal release of material can be observed in the cement and not a transformation. The signals interpreting these exothermal processess can be explained by the final burning of the eclosed organic material.

The DTA, DTG, TG relations of the structural components analysed and pre-

pared under identical circumstances differ from each other, but here, too, can be observed the thermoanalytical similarity of the cement and dentin layers and their difference from the enamel.

DISCUSSION OF RESULTS. CONCLUSIONS

On the basis of the instrumental analytical investigations carried out on the three structural components of the Loxodonta tooth, we may summarize our findings as follows:

1. The difference between the three layers can be revealed by means of optical, IR-spectroscopical, and derivatographic methods. Assuming the existence of the diversified structure variations directed by the taxonic situation, such a comparison of modern and fossiliferous taxons is justified. The thermoanalytic method can be recommended for the comparison of the complete tooth as an organic-inorganic unity, but carried out in different crucibles, and performing the inorganic control for the purpose of interpreting the thermoanalytical processes. [We deem it advi-

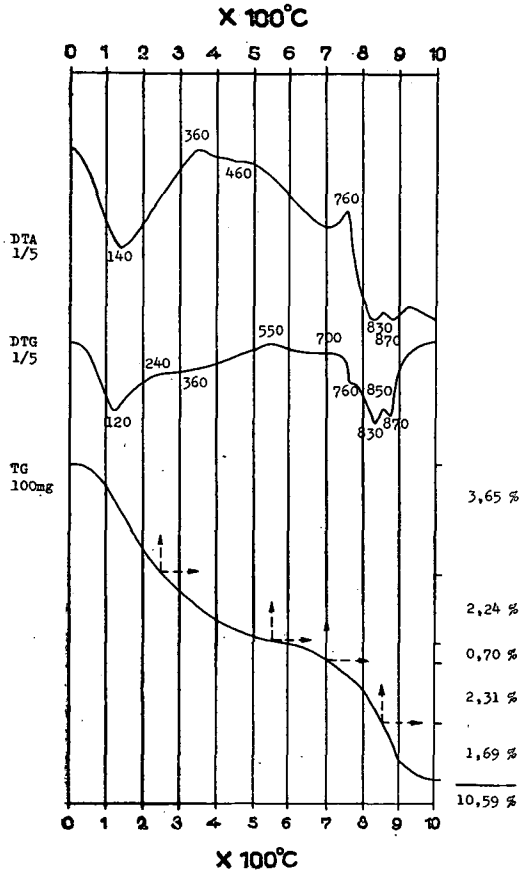

Fig. 18. The derivatogram of cement, previously treated with NaOH-glycerine, in a platinum crucible.

sable to perform the latter (inorganic control) investigation in inert atmosphere and to com pare it with the NaOH-glycerine method used by us]. The IR-spectroscopic analysis, following the above-described preparation method is suitable for tracing the organic fraction. For deciding problematic cases and investigating fine structures the optical method is the most suitable, first and foremost the replica-impression using D-3 condensor investigation. This comparative method will play an important role in the analysis of the teeth of small-size mammals and in the identification of fragment material.

2. Despite structural differences and slight physico-chemical deviations, the similarity of the cement and dentin layers is striking. This similarity is represented by both the IR-spectroscopic and the thermoanalytic series of investigations.

These facts prove that the cement layer is not an externally deposited dental calculi-like formation, but a calcified structure constructed by collagen, which must by all means be reckoned with in comparative taxonomic respect.

3. Though the employed methods differ, the human dentin and enamel derivatographic data of the Loxodonta, verifying the taxon-specific differences demonstratable between the various taxons.

4. For the first time in the course of analysing the teeth derivatographically we succeeded in outlining the thermoanalytic data of the inorganic phase satisfactorily. Naturally, the final solution will be the investigation of the samples in inert atmosphere.

5. In this form the thermoanalysis (derivatography) is suitable for tracing fossilization by means of absolute index numbers in connection with investigations on fossiliferous evolutional lines. In the course of similar research on organic and inorganic components it will be advisable to supplement the investigations with the analysis of the trace elements of the fossils and embedding sediment.

SUMMARY

The author has analysed the cement, enamel, and dentin layers of the molar tooth of modern Loxodonta africana by means of optical, IR-spectroscopic, thermoanalytical (derivatographic) methods. The investigations clarified the organic and inorganic chemical difference of certain structural components. On the basis of the results it may be assumed that comparative systematic, paleontologic (identification of fragment material) work can be carried out with the mentioned methods. Supplementing the derivatographic method with trace-element investigations, the procedure will also be suitable for expressing fossilization with absolute index numbers.

ACKNOWLEDGEMENT

The author expresses his gratitude to PROF. DR. MIKLÓS KRETZÓI (Dept. of Zoology, L. Kossuth University, Debrecen) for placing the investigation material at the author's disposal and for following the work with attention. The author thanks MR. ISTVÁN CSORDÁS (Dept. of Mineralogy, University for Heavy Industry, Miskolc) for the D-3 condensor pictures and MR. ZOLTÁN DINYA (Dept. of Organic Chemistry, L. Kossuth University, Debrecen) for preparing the IR-spectra.

REFERENCES

BERÉNYI M., MALATINSZKY, A. et IVÁNKIEVITZ, D. [1970]: A zománc és dentin termoanalitikai (derivatográfiás) vizsgálata. (Thermoanalitical study of enamel and dentine) — Fogorvosi Szemle **63**, pp. 40—43.

BOYD, W. C., BOYD, J. G. [1934]: An attempt to determine the blood groups of mummies. — Proc. Soc. Exp. Biol., N. Y. **31**, pp. 671—672.

BOYD, W. C., BOYD, L. G. [1937]: Blood grouping tests on 300 mummies. — J. Immunol., **32**, pp. 307—319.

CHALINE, J. [1959]: Utilisation du microscope electronique a balayage dans l'étude des dents de micromammiferes. — Mammalia **32**, pp. 211—218.

Дроздова Г. В. [1962]: Химическое исследование ископаемой кожи земноводного нижнепермского периода. – Доклады Академии Наук, СССР., **145** пп. 650-652.

GRAF, W. [1949]: Presence of a spasmogenic substance, presumably histamine, in extracts of mummy-tissue. — Nature **164**, pp. 701—702.

HELLER, W. [1966]: Biochemie und Feinstructur fossiler Knochen aus bituminösen Schichten. — Geol. Rundschau **55**, pp. 119—130.

KERNBACH, M. [1924]: Sur la présence d'une substance albuminoide dans les ossements anciens exhumés et sur sa propriété antigene. — C. R. Soc. Biol., Paris, **90**, pp. 1075—1077.

LIPTAY, G., BERÉNYI, M., SÁRKÁNY, E. [1969]: Ceramic crucibles in thermal analysis. — Hungarian Scientific Instruments **15**, pp. 31—35.

LOVAS, B. [1960]: Oberflächenuntersuchung mit dem Abdruckverfahren bei 3D-Kondensor-und Phasenkontrast-Beleuchtung. — Berichtigung in "Mikroskopie" **15**, pp. 1—18.

MCCONELL, D., [1938]: The problem of the carbonate apatites; a carbonate oxyapatite (dahllite). — Am. Journ. Sci., **236**, pp. 296—303.

MCCONELL, D. [1952*a*]: The problem of the carbonate apatites IV. Structural substitutions involving CO_3 and OH. — Bull. Soc. Franc. Min. Crist., **75**, pp. 428—445.

MCCONELL, D. [1952*b*]: The crystal chemistry of carbonate apatites and their relationships to the composition of calcified tissues. — Jour. Dental Res., **31**, pp. 53—63.

MCCONELL, D. [1960]: The crystal chemistry of dahllite. — Am. Min., **45**, pp. 209—216.

MOENKE, H. [1962]: Mineralspectren. (Aufgenommen mit dem Jenaer Spektralphotometer UR 10). — Akademie Verlag. Berlin.

PAULIK, F., PAULIK, J., ERDEY, L. [1958]: Ein automatisch registrierender Apparat zur gleichzeitigen Ausführung der Differentialthermoanalyse, der thermogravimetrischen und der derivativthermogravimetrischen Untersuchungen. — Z. Anal. Chem, **160**, pp. 241—252.

POSNER, A. S. et DUYCKAERTS, G. [1954]: Infra-red study of the carbonate in bone, teeth and francolite. — Experientia **10**, pp. 424—425.

PIEZ, K. A. [1961]: Amino acid composition of some calcified proteins. — Science **134**, pp. 841—842.

SCHRÄMLI et BECKER [1960]: Ber. Dtsch. Keram. Ges., **37**, pp. 227. (in Mackenzie R. C. 1962: "Scifax". Differential Thermal Analysis Data Index — St. Martin's Press. N. Y.)

SHACKLEFORD, J. M. et WYCKOFF, R. [1964]: Collagen in fossilis teeth and bones. — Ultrastructure Research **11**, pp. 173—180.

SILVERMAN, R., FUYAT, R. et WEISER, J. [1952]: Quantitativ determination of calcite associated with carbonate-bearing apatites. — Am. Miner., **37**, pp. 211—222.

SIMON, J., BALOGH, K., PETRUCZ, K. et ERDEY, L. [1969]: Thermal analysis of dental calculi and duct calculi. Periodica Polytechnica **12**, pp. 395—400.

SINEX, F. M. et FARIS, B. [1959]: Isolation of gelatin from ancient bones. — Sciences **129**, pp. 969.

STEPPUHN, O. et LYUBOWCOWA, X. [1930]: Proteolytische Zellfermente von ägyptischen Mumien (etwa 3000-jährig) und Mammut (etwa 30 000 bis 100 000 jährig) — Biochem. Z., **226**, pp. 237—242.

SZÖŐR, GY. [1969]: Molluszkum héjak aminosav, nyomelem, derivatográfiás elemzése. (Amino acid, trace element and derivatographic analysis of Mollusca shells) — Doktori értekezés (Thesis), Debrecen, KLTE.

SZÖŐR, GY. [1970]: Recens és fosszilis Mollusca héjak nyomelem vizsgálata. (Trace element determinations on recent and fossil Mollusca shells) — Acta Biol. Debrecina **6**. (In press)

SZÖŐR, GY. [1971]: Fáciesindikáció lehetősége Mollusca héj fizikai és kémiai vizsgálatával. (Possibilitis of facies indication by physical and chemical analysis of Mollusca shells) — Acta Geogr. Debrecina 1969/70. T. XV—XVI. (In press)

THIEME, F. P., OTTEN, C. M. et SUTTON, H. E. [1956]: A blood typing of human skull fragmenta from the Pleistocene. — Amer. J. Phys. Anthropol., **14**, pp. 437—443.
TOMES, J. [1850]: On the structure of the dental tissues of the order Rodentia. — Phil. Trans. Royal Soc. London, pp. 529—567.
YAMADA, K. [1934]: Proof of lipase in Peruvian mummies. — Chem. Abst., **31**, pp. 7074.
WYCKOFF, R. W. G. [1969]: Sur la composition de quelques protéines dinosauriennes. — C. R. Acad. Sc. Paris **269**, pp. 1489—1491.

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Acta Mineralogica-Petrographica, Szeged XX/1, 169 – 176, 1971

BOOK REVIEWS

I. KUBOVICS, GY. PANTÓ:

Vulkanológiai vizsgálatok a Mátrában és a Börzsönyben
(Volcanological Investigations in the Mátra and Börzsöny Mountains)
Akadémiai Kiadó, Budapest, 1970, 302 pages, 189 figures, 40 tables, 20 plates.

In the book the results of the geological-volcanological investigations of the Mátra and Börzsöny, two volcanic mountains of Hungary, are portrayed. Within the above subjects it is the chapters devoted to mineralogy and petrography that are elaborated in fullest detail. In other words, whereas the geology, geomorphology and magmatectonics of the two mountains are discussed in general terms, mainly on the basis of data from the literature in respect of the mineralogy and petrography of the Tertiary igneous rocks the authors report exhaustively on the large-scale investigations of their own which, however, did not encompass the two mountains as a whole.

Although the book has had to be split up into two main parts because of the presence of two separate mountain bodies, the two papers are nevertheless characterized by several common features which do not only justify their being published in one book, but do really forge them into one organic entity as well. Features of this kind can are: the means and methods of processing; adopting up-to-date volcanological principles; uniform terminology and usage of volcanological terms. Although being just a matter of form, the fact that the introduction is followed in both parts by a chapter on the history of investigations should be considered nevertheless to be a common feature. The afore-mentioned chapter is a rich summary of the major phases and results of investigations conducted prior to, or parallel with, the present author's research work by single specialists or groups of geologists. Similar accuracy and completeness characterize the list of references in geology and geography appended to each of the papers.

Part I. Mineralogical and Petrographical Investigations of the Northwestern and Western Mátra Mountains (by IMRE KUBOVICS). After an outline of the mountain's stratigraphy the Helveto-Tortonian volcanic complex is discussed in detail. The mainly andesitic effusive rocks as well as the andesitic, dacitic, rhyodacitic and rhyolitic pyroclastics are discussed in the order of succession of the eruptions forming two major units; the lower and upper volcanic complexes. Smallest units of discussion in the book are single formations, each being characterized by the identity of petrographic characteristics. As examples, let us quote the bronzitic pyroxene andesite or the andesitogenic potash trachyte or the dacitic tuff. The description of each formation of this kind includes data on the geographic situation and structural conditions of occurrence, its macroscopic and microscopic descriptions and, finally, the volcanological conclusions deduceable therefrom. These data are documented by photomicrographs, granulometric diagrams, mineralogical composition in volume

percentages, complete chemical analyses, eventual DTA-graphs, X-ray analyses, and summarizing tabulations. Petrography is followed by a separate chapter („Helveto-Tortonian Volcanism") summarizing the results of the author's petrological investigations in subchapter entitled *i „Orthomagmatic Paragenesis and Rock Texture"* and *ii „Hypo-Metamagmatic Paragenesis and Responsible Mineralogical-Petrographic Processes"*. As for the first group of questions (*i*), let us point out the series of alterations: orthopyroxene → pigeonite → augite → orthopyroxene; as for the second group (*ii*) including mineralizations (alterations) due to transvaporization, we should like to recall the process orthopyroxene → vermiculite → saponite; the formation of celadonite and glauconite; the production of potash trachyte from andesite and rhyodacitic tuffs by potash-metasomatism.

A short chapter portrays the collapse structure of the calderas of the volcanic mountains and the causes responsible for the development of the „periclinal" structure observable in the Mátra. With a view to the well known sedimentary basement of the mountains, the author considers the Mátra's caldera structure to be due to the combined effect of strata compaction (as verified by calculations) and of transvaporization.

The final chapter „Tectonic Conditions" given a summary of the data known from the literature and of the author's field observations in the light of the relationships between volcanism and tectonic processes.

Par II. „Tertiary Volcanism of the Northern Börzsöny Mountains" (by GYÖRGY PANTÓ). A general characterization of the geology of the mountains is followed by the main part discussing the petrographic conditions of the territory. In this part the volcanic formations are described in detail in two main groups: stratovolcanic complex and rocks connected with caldera formation.

The stratovolcanic complex is constituted essentially by andesites, andesitic tuffs with agglomerates, and andesitic agglomerates. Further subdivisions have been made on the basis of the mineralogical composition, with due consideration of the structural conditions. The same principle has been adopted in discussing, and making order among, the caldera formations characterizable by striking petrographic variability due to hypo- and endomagmatic influences. As a result of the author's investigations it has become possible to recognize such a zonal arrangement in which five major rock groups can be distinguished: *1.* intra-caldera stratovolcanics, *2—5.* subvolcanics connected with the caldera (sulphidic, iddingsitic-chloritic, calcareous-argillaceous-limonitic and, finally, oxyandesitic groups). The divergencies of the zones having close genetic connections indicate properly differences in the intensity of the metamagmatic effects to which they were subject. Descriptions of additional rocks occurring in the investigated — but not yet discussed — are to be found under the heading „Dike and Stock Formations at the Margin of the Caldera and on the West Mountain Border". Determinations of minerals and rocks were made by the use of optical instruments, chemical and spectral analyses, electron probe measurements, the author's special domain of activities, and, finally, with the aid of DTA and X-ray analyses. The results are illustrated with plates, tables, text-figures and photomicrograms. Beside the above investigations the author has aimed at characterizing the external habits of the individual rock variants, paying special attention to give their macroscopic descriptions and indicate exactly the sampling points.

As for the next chapter devoted to petrographic and geochemical evaluations, for lack of space, we cannot afford, unfortunately enough, to dwell on its valuable

content and logical construction. We must, however, quote those results which the author arrived at in elucidating and solving petrogenetical problems during his work. For the representation of the petrochemical conditions he has used the *AFM* diagram, confirming herewith the rightness of distinguishing three complexes for the Börzsöny Mountains volcanic formations. In the rest of the chapter the relationship between mineralogical composition, chemism, and textural characteristics are reviewed. A separate part is devoted to the description and interpretation of rock alteration phenomena due to hypo- and metamagmatic effects opacitization, uralitization, chloritization, „iddingsitization", carbonatization).

The final chapter is a short geohistorical review illustrated with a comparatively large—scale geological map and a geochemical map (representing the results of prospecting for trace elements) and geological profiles.

The two papers of the book are worthy continuations of the series fruitful of investigations into Hungary's Tertiary volcanism, looking back to great traditions. And we consider that they will fit well in and form material contributions to the geological monographs on the Mátra and Börzsöny Mountains which are to be completed soon.

DR. CS. RAVASZ

R. SEIM: *Minerale*

Neumann Verlag, Radebeul, 1970, 443 pages, 370 figures, 304 photos, 28 tables.

The ever-increasing circle of mineral collectors has gained powerful help by Professor SEIM's work. The book gives useful guidance to all friends of minerals who are not satisfied with the popular form of the recognition and loose systematization of the minerals but, striving at a deeper knowledge of the world of minerals, also search for answers to the questions „why" and „how".

In detail: the book can be both used as general mineralogy and for the recognition of minerals, i. e. the practical part is sufficiently supported by theory. This precept is determining in the arrangement of the subject, too.

The *first part* begins with the determination of the concept of mineral, and ends with the delineation of the main processes of the formation of minerals. Between these two end points, we get a picture of the habit and structure of crystals, their major types and laws, and the close relation between them.

The arrangement of the subject here — crystal morphology, mineral physics, mineral chemistry — is classic in its form, but shows the latest results as to its contents. This is followed by the petrological chapter leading on to the genetic part, which describes the major rocks within the framework of the nomenclature and systematization of the German-speaking countries. The last chapter gives a brief survey of the more and more firmly established rules of mineral collection, comprising the most important elements of field- and collection-work.

The *second part* of the book can be considered a key for determination as well as systematics. Minerals can be classified on the basis of four easily determinable characteristics: luster, colour, streak, and hardness. By the variation of these the author arranges the 282 minerals described in three main groups:

I. Minerals of metallic luster (the five sub-groups according to colour).

II. Minerals of submetallic and nonmetallic luster showing characteristic streak (the six sub-groups according to streak).

III. Minerals of nonmetallic luster the streak of which is grey, white, or which have no streak (the five sub-groups according to hardness).

The description of each mineral includes (according to sense) the following data: chemical composition, crystal system, hardness, density, the per cent quantity of its utilizable element, colour-streak, luster, transparency, habit (usually with the addition of one or several crystal drawings), the character of the crystal aggregate, cleavage, fracture and locality, similar minerals, further characteristics and accessory minerals, reference to photos in the book. This arrangement is really brilliant, also supported by the fact that one third of the more than three hundred photos are coloured.

The chapter "*The utilization of Mineral Raw Materials*" also provides a number of valuable data in a concise form, listed according to the alphabetic order of the name of each element: the finder of the element and the year of discovery, the volume of world production, the clark of the element, its crust average, the field its utilization, its important minerals with formulas indicating the type of formation.

An extra chapter deals with the industrial raw materials, and finally the precious- and semi-precious stones are summarized in a professional manner.

We hope that the present review is in itself sufficient to prove the utility, many-sidedness and still conciseness of the book. However, we want to call special attention to the excellent figures, being an organic supplement to textual parts seeming lexical or difficult to understand because of their nature: and, at the same time, insureing good entertainment to the *homo aestheticus.*

On summarizing we can say that the book fulfils our expectations we had when reading the subtitle (Enstehung, Vorkommen, Bestimmung, Verwertung), which are greatly helped by the easy-flowing style, clarity, and the high level of the technological design of the book.

DR. CS. RAVASZ

K. I. SZTRÓKAY, GY. GRASSELLY, E. NEMECZ, J. KISS:
Ásványtani praktikum I. (Mineralogical Practice. Volume I.)

Tankönyvkiadó, Budapest, 1971, 402 pages, 273 figures, 38 tables and 4 coloured plates.

The purpose, structure and applications of the book are the same as those of the second volume published in the previous year (and reviewed by us, too). That is why there is no need to repeat its evaluation and review here. As for the content of the volume, however, let us emphasize that is primarily characterized by the predominance of the conventional methods of determinations of minerals — declared, very often, to be simple — which largely increases the value of the book. At the same time, the present volume gives information providing a sound basis for making the most useful choise among of the research facilities listed in Volume II and, consequently, for undertaking further measures.

Before entering into details in respect of the investigational method, in the individual chapters of the book the authors first review the applications of the particular techniques, and then proceed to a regular description of the instruments, devices and reagents and to give some practical advices and instructions on the rules to be adopted. According to the didactical principle, the understanding of the problems is facilitated exercises expounded fully, and in many cases the method is demonstrated by the direct solution of quite a number of tasks.

The individual chapters embrace the following subjects.

The chapter entitled "*Crystallographic Measurements, Calculating and Constructing Operations*" is a very detailed treatise accounting for almost one-third of the total volume of the book. It has been split up into four subchapters: in the first one, "The External Form of Crystal" the fundamental conceptions and laws of crystal morphology as well as goniometric measurements are discussed and afterwards the measured data are represented in projections as exemplified by the individual crystal systems. The second subchapter includes calculations of crystal elements and the relevant calculations of spherical trigonometry. Next to follow is a subchapter on the construction of the projectional (gnomonic) crystal-drawing. The final subchapter is devoted to a discussion of the principles and operations for direct crystal drawing method — the method of plane intersection.

The second chapter, "*Investigations in the Domain of Physical Properties*", gives a description of the main operations of routine work on determining minerals — operations that can be carried out with the aid of a rather simple equipment, paying due attention to explain and define the basic, theoretical, relationships of the physical properties of the minerals and the causes responsible for them. In this chapter information is given about measuring of the density, cleavage, hardness, glinding (translation), and carrying out spectral analyses and scratch tests and finally, about the application of blow-pipe.

"*Simple Chemical Reactions*" is the title of the chapter discussing the traditional determination operations in mineral chemistry, where express methods for detecting of the most important cations and anions are described in the following groups: tests with borax and phosphate beads; production of coatings, sublimates and metallic globules; simple chemical reactions (hepar sulphuris); staining techniques (carbonate minerals, feldspars, etc.).

"*Microchemical Reactions*". In this chapter the techniques for producing drop reactions are summarized and then their applications are discussed. First the operations with the most usual reagent solutions (Montequi solution, CsCl, KI, $TlNO_3$, etc.) and then the reactions of the individual elements (groups of elements) are discussed. The photomicrographs of the reaction products (crystallites) totalling 96 in number are a great advantage of this chapter.

"*Colour Reactions, Semi-Microanalyses*". A discussion of the main points and instruments of this method, still of restricted use in Hungary, is followed by a detailed description of qualitative microanalytical operations. The elements considered to be important for geology (from the geological point of view) are listed according to a classification in siderophile, chalcophile and lithophile groups. The discussion of the reactions for detecting the individual elements is preceded by a short geochemical summary in which the frequencies and characteristic minerals of the respective elements in the individual geophases are reviewed. Illustrations to the chapter coloured plates on four pages, have been appended to the book.

"*Paper Chromatography*". Like in the two previous chapters, such a method is described here which would be very useful to propagate more widely in the practice of mineral determinations. Therefore, the comparatively long introduction is to be welcomed here. The author has made efforts to demonstrate chromatography based on separation, relying mainly on H. Agrinier's data. The part devoted to methodology cannot be reviewed here, but we should like to point out that the small tabulations compiled for ease and clearness in the qualitative and semi-quantitative (quantitative) determinations of single groups of elements (elements, RF value, colour reactions) are well-suited to the purpose.

"*Mineralogical Calculations from Chemical Analyses.*" Even though small in volume, this chapter is very significant, for it gives a selection of the most important methods for coordinating and comparing the results of mineralogical, petrographical and chemical investigations. Thus the reader can get acquainted with the operations for calculating mineral formulae from the chemical analyses of relatively homogenous minerals and for determining the ratios of the constituents of mixed crystals. The next subchapter describes the ways in which volume percentages, weight ratios and weight percentages can be calculated from linear measurements on thin- and polished sections of rocks and ores. We cannot agree, however, with its title: "Determination of the Volume Ratios and Weight Percentages of Mineral Components in Ore and Rock Texture" because of the improper use of the term texture. Very timely is the subject of the correlation calculations discussed in the following chapter. In addition, the outlining of the characteristics of isomorphous substitutions and coordination numbers which can be expressed in terms of the chemical (stoichiometric) formulae of the minerals, is greatly appreciated. Finally, examples are given to illustrate calculations for developing formulae in crystal chemistry calculations gradually gaining in importance nowadays.

At the end of each chapter there is a list of references, and the book itself ends with an exhaustive index of names and subjects.

Summarizing the appraisment of the book, let us state that is provides very useful informations in a form easily intelligible. The selection of its contents is very lucky, as authors have managed to couple the commonest research methods with the majority of techniques which would deserve to be disseminated more widely.

The editing and the typographical execution of both volumes have hit high standards. Thus, with a view to both content and form, it is hoped with good reason that the book may become one of the most popular representatives of the Hungarian-language publications in mineralogy.

DR. CS. RAVASZ

SZÉKY—FUX V.:

Ore Formation of Telkibánya and its Connections to the Carpathians.

Publishing House of the Hungarian Academy of Sciences, 1970, 266 pages, 60 figures, 79 tables, 15 supplements, (in Hungarian, with an English resumé)

A new book of nice get-up was published on the ore formation and its farther connections of Telkibánya belonging to the Tokaj Mountains and which had been more famous in previous centuries. The former researchers dealt with the investigation of the vein-containing formations and of the qualitative and quantitative relations of the ore paragenese; insignificant attention was focussed on rock metamorphism accompanying the ore formations, this was considered as accessory phenomenon. It is well-known, however, that between the formation and evolution of the ore-transporting and ore-admitting rocks and the development of the ore formation there is for the most part a strong connection. On this basis each of the endogeneous ore formations amounts to each petrogenetic evolution phase of the igneous rocks. Consequently, between the igneous rocks and the ore formations of them there is a close connection, the one develops with gradual transition from the other, i. e. these are petro-metallogenetic series. These petrogenetic series and their evolution were investigated by the author.

On the basis of the intention the book is divided into four chapters.

The first chapter deals with local geological fundamentals, magma-genetic and tectogenetic conditions determining the ore formation. In this chapter informations are given on the place of occurrence within the Alp-Carpathian metallogenetic province, on the history of the area's geological knowledge and, on the basis of the results of the latest investigations, on the geological structure of the ore-containing area of Telkibánya. These statements are based for the most part on the investigation results of E. Scherf and author.

The second chapter discusses the petro—metallogenesis of the ore formation. The detailed petrological investigations, from the hypo- and meta-transformations to the mineral and trace element parageneses of the veins resulted in the recognition of those processes which played singificant role in leaching the floor of the volcanites, in mobilizing the ore substance, in developing the veins and in forming the volcanites themselves. These processes and the factors activating them, respectively, are separated into ascendent and descendent processes, according to their direction and character. On this basis author distinguishes the processes which precede (pre-metallogenetic), accompany (syn-metallogenetic) and follow (post-metallogenetic) the ore formation, and proves the originated parageneses.

In the course of the discussion of the pre-metallogenetic processes author introduces particularly the mineral and chemical composition of the Sarmatian pyroxene-andesite. Discussing the petrogenetic development she describes the rock alteration of the single mine adits and galleries. A lot of data relating to alkali and SiO_2 content of the rocks are published, and the newly developed mineral assemblages are also described. In every cases she establishes the petro-metallogenetic series and the mobile components, respectively.

Discussing the syn- and post-metallogenetic processes author describes the genesis of the andesitogenetic potash-metasomatites and determines the petro-metallogenetic series, the mineral composition of the rocks as well as the mobile components. Results are supplemented by data of X-ray investigations and chemical analyses. The hydrothermal processes accompanying or following the potash-metasomatism result in the subsequent endo-meta-transformations and petro-metallogenetic evolution of the rock. The petro-metallogenetic series of carbonation, silification, pyritization, sericitization and their mobile components, appearing under such conditions, are proved by concrete precedents supplemented by DTA and X-ray investigation results. The investigation results of the oxidation zone and clay mineralization terminate this chapter.

The third chapter deals with the metallogenesis and characterizes the veins and ore-zones. The veins of the Gyepü and Kánya Mountains as well as the general characterization of the local ore formations are discussed separately.

From the point of view of the geological development of ore-content, the veins of the Gyepü Mountain can be divided into four groups. The gaping fissures of silicic-clayey formations with pyrite-marcasite bands and abundant silica-content may be assigned to the first group. The silicic-pyritic, silicic-ochre-containing, pyritic-clay mineral-containing veins belong to the second group. These are not characteristic fissure-filling substances but originated in the fracture zones of the subsequent movements. The pyritic-ochre-containing bands with noble metal content, being of parallel strike with the second group's members, constitute the third type, while the fourth assemblage contains sphalerite with carbonaceous-clayes filling substance.

On the basis of the formation and filling—up the veins of the Kánya Mountain can be assigned to three types. The veins which can be separated from the associated

rock by a determined plane, belong to the first type. Their filling substance is of pyrite which is accompanied by other coloured sulphides as well as by silicic and often clay minerals. More considerable noble metal content can be observed only in the pyrite-rich part of the veins. The veins constituting the second group cannot be sharply separated from the associated rock, they are not vein fissures but are silicic zones grey coloured by colloid pyrite. These veins are characterized by considerable pyrite and noble metal content. The veins belonging to the third type are of quartz-ocher rarely of clay-ocher and are characterized by determined separating planes.

The description of the veins of both the Gyepü and the Kánya Mountains is supplemented by numerous chemical analyses as well as by trace element and DTA investigations.

The third part of this chapter gives a general review of the ore formation. Both the geochemical interpretation of the trace element investigations and the temperature of the ore formation of Telkibánya, as well as the ore formation of the deeper-lying Tortonian andesites are described. Finally, on the basis of the leaden-isotop investigations concerning the age and genesis of the ore formation, author states that in the area of Telkibánya two phases of ore formation can be distinguished: epi-mesothermal ore formation containing noble metals and pyrite lying in a higher level, on the one hand; and an older mesothermal one of Pb-Zn-Cu formation lying in a deeper level, on the other.

The fourth chapter deals with the petro-metallogenesis of the hydrothermal ore formation of the Inner Carpathian Neogene Ore Province. The ores of the Dunazug, Börzsöny, Mátra and Selmec Mountains and those of the Hilly Country of Beregszász are characterized in general. In the part entitled "Metallogenesis of the Transylvanian ore deposits" the general features of the ore formations of the Gutin and Hargita Mountains, the Transylvanian Ore Range, as well as of the Kelemen and Görgény Alps are described.

This work is worthy of note because from the metasomatic point of view author summarizes at first the ore formation of Hungary's one mining districts on the basis of the mineralogical-petrological, geological, geochemical and metallo-geological data and this initiative may promote the further ore researches in the future.

Doc. Dr. J. Mezősi

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LETTERS OF THE WORKING GROUP ON MANGANESE FORMATION OF INTERNATIONAL ASSOCIATION ON THE GENESIS OF ORE DEPOSITS

MEMORIAL OF DONNEL FOSTER HEWETT

JOHN VAN N. DORR

DR. DONNEL FOSTER HEWETT died on February 5, 1971 in Menlo Park, California. He was approaching his 90th birthday.

DR. HEWETT, called Foster by his many friends and admirers, contributed a great deal to our knowledge of the mineralogy and geology of manganese not only through his own immense energy, deep knowledge, and scientific skills but perhaps even more by mobilizing many able men to study the deposits of this element throughout this country and Latin America during the periods when he could devote little time to the subject himself owing to administrative duties .

He graduated from Lehigh University in 1902 as a mining and metalurgical engineer and was in commercial work until 1911. During this period he was responsible for the development of the famous Minas Ragra vanadium deposit in Peru, for many years a principal source of vanadium in the world. He received his PhD in geology from Yale in 1924 and a Honorary Doctor of Science degree from Lehigh in 1942. He served twice as Vice President of the Geological Society of America and as Vice President and President of the Society of Economic Geologists, as well as Distinguished Lecturer of the latter organization. He was a member of the National Academy of Science.

His career with the United States Geological Survey began in 1911 and continued in positions of ever increasing responsibility until serious illness in 1944. This, however, was not the end of his active career with USGS; he continued work until a month before his death. The years after his retirement from administrative work were the most productive ones from a scientific viewpoint; relieved from administrative responsibilities, he could concentrate on field work and on laboratory research, in the course of which the large bastnäsite deposits of the Mohave desert were discovered and a number of important papers on manganese were produced.

The files and specimens in his Menlo Park office are an extraordinary monument to his wide-ranging interest in and knowledge of the manganese occurrences of the world and to his far-flung correspondence with scientists of many countries working on this element.

Hewett's most lasting contribution to the science of geology was perhaps in bringing forward, stimulating, and giving wise guidance to a large number of young men, now at the apices of distinguished careers of their own. He was a very human man, loved for his strengths and for his foibles alike. His extraordinary productivity in later years and his wisdom and kindness will always be an inspiration to those who knew him.

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LETTERS OF THE WORKING GROUP ON MANGANESE FORMATION OF INTERNATIONAL ASSOCIATION ON THE GENESIS OF ORE DEPOSITS

PROGRESS REPORT ON RESEARCH IN MANGANESE ORE DEPOSITS OF ROMANIA (1956—1970)

RADU DIMITRESCU

Large scale investigations on manganese ore deposits began in Romania in 1954. The production of manganese jumped from 59130 t. in 1948 to 389921 t. in 1955. Since the first comprehensive report delivered by V. IANOVICI in 1956 at the first Symposium on manganese deposits (6), more than 20 papers were published in this country concerning the mineralogy, petrology, geochemistry and structure of Romanian manganese ores.

As a result of a first series of investigations, the mineralogical composition of the ores was established. The primary ores are metamorphic, being synchronous with the crystalline schists of the Carpathians; they consist of manganiferous carbonates rhodonite, bustamite, pyroxmangite, tephroite, knebelite, spessartinite, dannemorite, Mn-anthophyllite, jakobsite, piedmontite; secondary ores of the oxydation zones consist of neotokite, hisingerite, manganite, coronadite, cryptomelane, hausmannite, pyrolusite. Optical constants were accurately determined for a part of these minerals [D. RĂDULESCU, H. SAVU, L. PAVELESCU, R. DIMITRESCU etc.].

A further development of the same investigations was the determination of the constitution of minerals representing isomorphous series in various deposits. Jakobsite, pyroxmangite, spessartinite, and bustamite from the Sebes Mts [L. PAVELESCU], as well as Mn-carbonates (rhodochrosite-ponite), rhodonite, pyroxmangite and spessartinite from Iacobeni [G. POPA] were analysed.

The chemical composition of the ores was the object of numerous investigations. The geochemistry of the deposits was interpreted by means of graphical statistics in a first period [M. SAVUL, V. IANOVICI, C. DRĂGHICI], afterwards analytical statistic methods being extensively used by V. IANOVICI, AL. DIMITRIU and POPA.

As a result, the primary genesis of a large part of the metamorphosed deposits is now understood as being sedimentary — volcanogeneous.

Structural research was carried out by R. DIMITRESCU in the Iacobeni area, where shear-folding was substantiated by petrofabric analysis.

REFERENCES

FL. CODARCEA and V. CODARCEA: Contributions to the Mineralogical and Genetical Study of the Siliceous-Manganiferous Rocks of South-Eastern Banat. — S.S.N.G. — Com. Geol. **27**/3—4, Bucuresti, 1962.

R. DIMITRESCU: Note sur la structure du cristallin de la région Iacobeni — Inst. Geol., D. d. S. **51**/1 (1963—64), 15—29, Bucuresti, 1965.

C. DRĂGHICI: Contributions à l'étude des silicates de manganèse et de fer dans les monts du Sebes — Inst. Geol., Stud. Tehn. Econ. **A6**, 177—199, Bucuresti, 1969.

C. DRĂGHICI, G. HRISTESCU, M. SBARCEA: Contributions à la connaissance du gisement de manganèse de Delinesti (Banat) — Inst. Geol., Stud. Tehn. Econ. **A7**, 223—241, Bucure ti, 1967.
D. GIUŞCĂ: Contributii la studiul mineralogic al zăcămintelor de mangan de la Răzoare şi Delineşti. — Stud Cerc. Geol. 7/3—4, Bucureşti, 1962.
V. IANOVICI: Sur les gisments de minerai de manganèse de la Roumanie. Symposium sur les gisments de minerai de manganèse. — Travaux de XX-ème Congrès International Geologique. Mexico, 1956.
V. IANOVICI, AL. DIMITRIU and C. IONESCU: Studiul geologic şsi geochimic al zăcămintelor de mangan Dadu şi Coşna (Carpaţii Orientali) — Stud. Cerc. Geol. **11**/1,115—141 Bucureşti, 1966.
V. IANOVICI, AL DIMITRIU, D. CONSTANTINOF, C. DRĂGGHICI, C. IONESCU: Les caractèreŝ distinctifs chimico-mineralogiques des minerais de manganèse de la R.S. de Roumanie — Assoc. Carp. Balk., VIII-e Congrès. Vol **II**, 235—245, Beograd, 1967.
V. IANOVICI, D. CONSTANTINOF, C. DRĂGHICI, C. IONESCU and AL. DIMITRIU: Geology of Manganese Deposits in Rumania. — XXIII. Intern. Geol. Congr., vol **13**, 269—278, Prague, 1968.
V. IANOVICI et AL. DIMITRIU: Considérations sur la genèse des gisments de manganèse des monts de Sebeş. — Stud. Cerc. Geol. **13**/1,25—32, Bucureşti, 1968.
V. IANOVICI and AL. DIMITRIU: Geochemical Parameters of Ores in the Socialist Republic of Romania. I. Distribution of Main Chemical Elements in Manganese Ores. — Stud. Cerc. Geol., **13**/1,3—15, Bucureşti, 1968.
V. IANOVICI, AL. DIMITRIU, A. ANDĂR: Parametrii geochimici ai minereuirilor din România. II. Corelaţia şi regresia dintre elementele chimice principlae în minereurile de mangan. — Stud. Cerc. Geol. **14**/1, Bucureşti, 1969.
V. LAŢIU: Contribution à l'étude micrographique et génétique des mineraux manganifères du gisement de Răzoare (Transylvanie) — Bul. Inst. Polit., **2**, 3—8, Timişoara., 1956.
L. PAVELESCU: Consideraţii mineralogice asupra unor şisturi cu silicaţi de mangan şi fier din Munţii Sbeşului. — Comun. Acad. R.P.R. **5**/2, 369—376, Bucureşti, 1955.
L. PAVELESCU et M. PAVELESCU: Etude cristallochimique de certains minéraux de manganèse des monts Sebeş. — Inst. Geol. D. d. S **55**/1, (1967—68), 13—31, Bucureşti, 1970.
GH. POPA: Studiul mineralogic, petrografic şi geochimic al zăcă mintului de minereu de mangan din regiunea Sarul Dornei şi Dealul Rusului. Teză de doctorat I.P.G.G., Bucureşti, 1971.
D. RĂDULESCU and V. IGNAT: Neotokit in den Manganerzen von Jakobeny N. Jb. Min. Mh., **2/3**—1958, 55—85, Stuttgart, 1958.
D. RĂDULESCU: Contributionsà la connaissance des minèraux des gisments de manganèse de la Moldavie du Nord. — Inst. Geol., D.d.S. **43** (1955—56), 11—26, Bucureşti, 1962.
D. SANDU: Contributions to the Study of the Manganese Oxides in Suceava Region. — Bul. I.P.G.G., **6**, 39—64, Bucureşti, 1958.
H. SAVU: Contributions à la connaissance des gisements de manganèse de la région de Delineşti (monts Semenic). — Inst. Geol., D.d.S. **46** (1958—59), 147—154, Bucureşti, 1962.
M. SAVUL şi V. IANOVICI: Chimismul şi originea rocilor cu mangan din Cristalinul Bistriţei. — Bul. St. Geol-Georg. **II/1**, 119—169, Bucureşti, 1957.
M. SAVUL şi V. IANOVICI: Chimismul rocilor cu mangan din Carpaţii Orientali şi Meridionali din R.P.R. — Stud. Cerc. Geol. 3/1—2, 7—60, Bucureşzi, 1958.

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LETTERS OF THE WORKING GROUP ON MANGANESE FORMATION OF INTERNATIONAL ASSOCIATION ON THE GENESIS OF ORE DEPOSITS

REPORT ON RECENT WORK IN MANGANESE ORE RESEARCHES IN CZECHOSLOVAKIA (1966—1970)

LUBOR ŽAK

In the last years, it was especially the Algonkian manganese carbonate and pyrite deposit of Chvaletice (E. Bohemia), where new studies on mineralogy and paragenesis have been made.

Detailed mineralogical studies on helvite [F. ČECH and P. POVONDRA, 1969], axinite and Ba-adularia [V. HOFFMAN and F. NOVÁK, 1966], dravite F. NOVÁK and L. ŽÁK, 1970], pyrophanite [L. ŽÁK, in print], and melanophlogite [L. ŽÁK, 1967; in preparation] have been made. Some further Mn-silicates from the deposit are under study. The research of sedimentary and vein Mn-carbonates will also be completed.

As far as concerns the minerogenesis, a new conception of metamorphic processes has been elaborated [L. ŽAK, 1970, 1971]. The sedimentary syngenetic manganese-pyrite ores, genetically connected with a basic initial geosynclinal volcanism, were subjected to a regional epizonal hydrothermal metamorphism. The processes were due to an intraalgonkian phase of the Assyntian orogenesis from a great part. The hydrothermal metamorphism of the ore deposit was most intensive in a tectonic zone, rimming the Chvaletice granite massif. The granite massif follows an important NW-SE tectonic line between the epi- and mesozonally metamorphosed Proterozoic rocks. It is pegmatite-defficient and hydrothermally metamorphosed together with the hanging wall Algonkian sediments. No minerals documenting a temperature above 500° C in the direct granite contact have been observed. The hydrothermal metamorphism of the ore deposit produced fine-grained hornstones with Mn-silicates, pyrite, pyrrhotite etc. and the vein minerals, including Mn-carbonates, Mn-silicates, sulfides and oxides as well. Three etaps of metamorphism can be distinguished, the last one being of a low temperature, Alpine paragenesis type. The succession on veins documents subsequent metamorphic mobilization of the major (Mn, Fe, C, S) and minor or trace (Si, Ti, B, Be, As, Cr, Zn, Pb, Cu etc.) elements of the ore. Metasomatic vein mineral replacements are frequent. The temperature interval from the first metamorphic etap, following the granite intrusion probably, to the third one was estimated to have been between 400 and 100° C. probably. The last etap may be younger than Algonkian.

REFERENCES

ČECH F., POVONDRA, P. [1969]: Helvite from hydrothermal veins at Chvaletice, Bohemia. — Acta Univ. Carol., Geol., 1—11.

HOFFMAN V., NOVÁK, F. [1966]: Axinite and Ba-adularia from Chvaletice in the Iron Mts. — Sbor. Nár. Muz., Praha, **22B**, 27—46. In Czech.

NOVÁK, F., ŽÁK, L. [1970]: Dravite asbestos from Chvaletice. — Acta Univ. Carol., Geol., 27—44.

ŽÁK, L. [1967]: Find of pyrophanite and melanophlogite in Chvaletice (E Bohemia). — Čas. Mineral. Geol., **12**, 451—2.

ŽÁK, L. [1970]: Minerogenetic units of the north-western part of the Iron Mts. — Čas. Mineral. Geol., **15**, 181. In Czech.

ŽÁK, L. [in print]: Pyrophanite from Chvaletice. — Mineral. Mag.

ŽÁK, L. [in preparation]: A contribution to the crystal chemistry of melanophlogite. — Amer. Mineral.

ŽÁK, L. [1971]: Mineralogical and genetical research of the Chvaletice-Litošice deposit in the Iron Mts. Praha, unpubl. Final report on research. In Czech.

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